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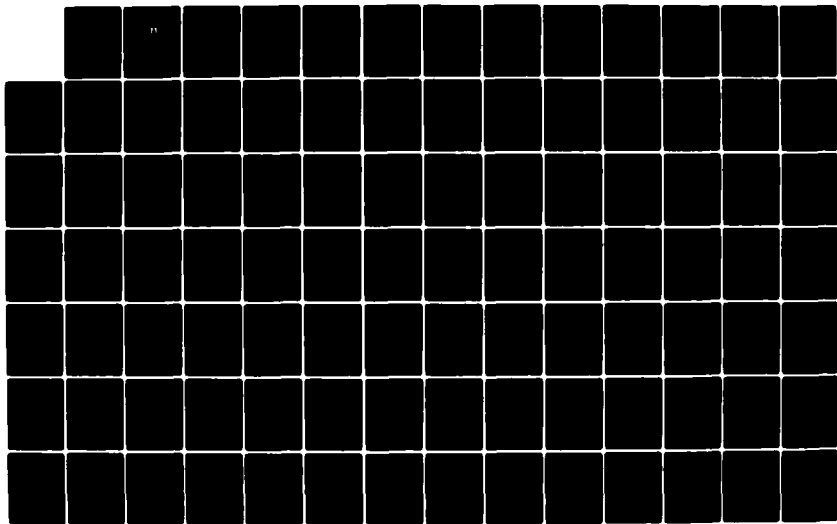
STANDARD METHOD FOR ANALYZING GASES IN TITANIUM AND  
TITANIUM ALLOYS STAND... (U) FOREIGN TECHNOLOGY DIV  
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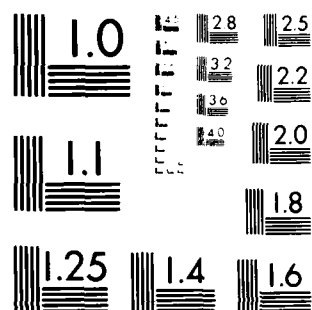
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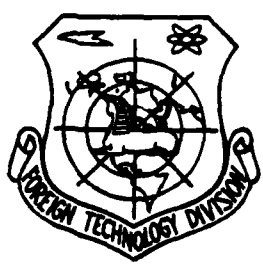
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# FOREIGN TECHNOLOGY DIVISION



STANDARD METHOD FOR ANALYZING GASES IN  
TITANIUM AND TITANIUM ALLOYS

STANDARD METHOD FOR THE CHEMICAL ANALYSIS  
OF TITANIUM ALLOYS



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## EDITED TRANSLATION

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WP.AFB, OHIO.



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#### GRAPHICS DISCLAIMER

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GENERAL PRINCIPLES FOR THE STANDARD METHOD  
OF ANALYZING TITANIUM AND TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

1. This standard is applicable for measuring titanium alloy chemical components used in aviation. When there is arbitration analysis, it is necessary to use a fixed method according to this standard.

2. The sample used for analysis must be handled according to the pattern of the sample. Prior to processing, eliminate the oxidizing layer on the surface of the sample. A milling machine is used for cutting the thickness to no larger than 0.1 millimeters and the length no larger than 10 millimeters.

3. The pure metal or metallic oxide used to make up the standard solution should have over 99.90% purity or spectral purity. If we use a standard solution made up of a compound or common pure metal, its accurate density must be determined by a weight method or standard substance.

4. The reagent purity used for analysis generally does not have clear specifications and the "water" is commonly water distilled once or de-ionized water of equal purity. The "solution" is an unspecified water solution.

5. The indicating method for the reagent density is:

A solid reagent is generally composed of a weight-volume

ratio which is indicated by %. For example, 20% sodium hydroxide indicates 20 grams of sodium hydroxide dissolved in 100 milliliters of water.

A liquid reagent is generally made up of volume and is expressed by % or volume ratio. For example, 2% nitric acid is 2 milliliters of nitric acid combined with 100 Milliliters of water, and 1:2 hydrochloric acid is one volume of hydrochloric acid combined with 2 volumes of water.

6. The hot water or hot solution system used for analysis is 60-70°C water or solution. The temperature system of the warm water or warm solution is 40-50°C water or solution.

7. It is necessary to correct capacity instruments and other measuring instruments as well as the photometer's wavelength prior to use.

8. When measuring each element, there must be at least three equally analyzed fractions. The deviations of the analysis results should be within the allowable error range and its mean value is counted as the final analysis results.



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# STANDARD FOR THE DETERMINATION OF ALUMINUM IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

## The EDTA Volumetric Method

### 1. Summary of Method

In a sulphuric acid solution, a cupferron reagent and copper reagent are used to precipitate the titanium, tin, vanadium, iron and zirconium, and trichloromethane is used for extraction and separation. In a solution where the pH=2-3, when we add an EDTA solution and aluminum complex, EDTA solution is excessive. When in a pH=5-6 acetate acid solution, we take PAN as the indicator and use a copper sulphate solution for titration. If added into sodium fluoride, the EDTA complex further uses a copper sulphate solution for titration of the released EDTA. The aluminum content is calculated based on the amount used in the second copper sulphate solution.

Measurement range: 2.00-8.00%.

### 2. Reagent

Sulphuric acid	: 1:1
Nitric acid	: proportion 1.42
Ammonia water	: 1:1
Copper reagent	: 20% solution
Cupferron reagent	: 10% solution
Dimethyl phenol orange	: 0.2% solution (newly made filter used)
PAN indicator	: 0.2% alcohol solution
Trichloromethane	:
Sodium fluoride	: solid

Sodium acetate buffer solution (PH5-6): 2M. 60 grams of anhydrous sodium acetate are dissolved in water, add 4.5 milliliters of glacial acetic acid and dilute with water to 500 milliliters.

EDTA standard solution: 0.025M. 9.30 grams of sodium ethylenediaminetetra-acetic acid are dissolved in water, diluted to 1,000 milliliters with water and shaken evenly.

Copper sulphate standard solution: 0.0125M. 17 grams of copper sulphate are dissolved in water, diluted to 1,000 milliliters and shaken evenly.

Aluminum standard solution: take one gram of pure aluminum (99.99%), 20 milliliters of 40% sodium hydroxide solution, heat until dissolved and cool. Neutralize with 1:1 sulphuric acid until acidity exceeds 20 milliliters and cool. Transfer into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly. Each milliliter of this solution contains 1 milligram of aluminum.

The following method is used to determine the titration of the copper sulphate standard solution on the aluminum.

Put 0.1 grams of pure titanium in a 250 milliliter beaker, add 5-10 milligrams of aluminum standard solution, add 10 milliliters of 1:1 sulphuric acid, .... and carry out according to the analysis procedure.

The titration of the copper sulphate standard solution on aluminum is expressed by T and is calculated according to the following formula:

$$T = \frac{g}{v}$$

In the formula: g is the weight (milligrams) of the aluminum in the aluminum standard solution; v is the volume (milliliters) of copper sulphate standard solution consumed during titration.

### 3. Analysis Procedure

0.1 grams of the sample are placed in a 250 milliliter beaker and after adding 10 milliliters of 1:1 sulphuric acid and heating until melted, we drip in nitric acid and oxidize until the solution's purple color disappears. Continually heat and evaporate until the sulphuric acid emits smoke for 1-2 minutes. After cooling, wash the beaker wall with water. Shift into a 125 milliliter separatory funnel and shake evenly (volume is about 25 milliliters). Add 20 milliliters of a 10% test solution of copper-iron, 5 milliliters of 20% copper test solution, 30 milliliters of trichloromethane, shake for two minutes. After it has settled into layers, remove the organic phase, and again add 10 milliliters of trichloromethane, shake for one minute, after it has settled into layers, remove the organic phase, repeat this once more and place the water phase into a 250 milliliter conical flask and wash the separator funnel with water. Heat the solution and boil for 2-3 minutes, cool a little and then add 10-15 milliliters of EDTA standard solution and 2 drops of 0.2% dimethyl phenol orange solution neutralized by 1:1 ammonia water until the solution assumes a purplish red color. Further, add 1:1 sulphuric acid until the purplish red color turns yellow. After adding another one drop, heat and boil for 2-3 minutes and then add 5 milliliters of sodium acetate buffer

solution and drip in 6-8 drops of 0.2% PAM indicator. Use the copper sulfate standard solution for titration until the solution changes from yellow green to purple. Add in 0.5 grams of sodium fluoride, boil for 1-2 minutes, add two drops of 0.2% PAM indicator and then use the copper sulphate standard solution for titration until the solution changes from yellow green to purple.

#### 4. Calculations

The percentage content of aluminum is calculated by the following formula:

$$Al\% = \frac{T \cdot V}{G} \times 100$$

In the formula, T is the titration (milligrams/1 milliliter) of the copper sulfate standard solution for the aluminum; V is the volume (milliliters) of copper sulphate standard solution consumed during the second titration; G is the weight (milligrams) of the sample.

#### 5. Allowable Deviation

Aluminum Content %	Allowable Deviation %
2 - 4	$\pm 0.05$
4 - 8	$\pm 0.10$

Note 1: The quantity of EDTA used should be based on the increase and decrease of the contents. Each milliliter of 0.025 MEDTA solution is equivalent to 0.68 milligrams of aluminum.

Note 2: The cupferron used must have guaranteed quality. For example, when it has absorbed water or changed color it cannot be used.

Note 3: When the chromium content in the sample is larger than 5%, after dissolving, add 5 milliliters of perchloric acid, heat until smoke appears and there is a reddish brown color and then drip in hydrochloric acid to expel the chromium. Finally, add a small amount of sodium chloride so that after the chloride is completely volatilized we proceed according to the analysis procedure.

Note 4: When the manganese content in the sample is greater than 2.5%, the last point of titration is not sensitive and the results are not stable. The manganese content in titanium alloys is generally greater than 2.5% and thus does not affect the determination of the aluminum.

STANDARD FOR THE DETERMINATION  
OF VANADIUM IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

I. The Ferrous Sulphate Volumetric Method

1. Summary of Method

In a sulphuric acid medium, a potassium permanganate is used to oxidize the four valence titanium into five valence titanium. When there is urea, excessive potassium permanganate is reduced by sodium nitrate. Afterwards, the phenyl substituted amino benzoic acid is the indicator and the ammonium ferrous sulphate standard solution is used for titration until the solution changes from purple to green. We calculate the vanadium content based on the amount of ammonium ferrous sulphate standard solution consumed.

Determination range: 1.00-10.00 %

2. Reagent

Sulphuric acid: 1:1  
Nitric acid : specific weight 1.42  
Potassium permanganate: 10% solution  
Sodium nitrate: 1% solution  
Urea : Solid

Phenyl substituted amino benzoic acid indication: a 0.2% solution is dissolved in 100 milliliters of water and added into 0.2 grams of phenyl substituted amino benzoic acid and 0.2 grams of anhydrous sodium carbonate and dissolved by

heating.

Potassium dichromate standard solution: 0.1N. 4.903 grams of standard potassium dichromate are placed in a 200 milliliter beaker. After being dissolved by a small amount of water it is transferred into a 1,000 milliliter volumetric flask, diluted to calibration and shaken evenly.

Ammonium ferrous sulphate standard solution: 0.05N. 10.51 grams of ammonium ferrous sulphate are dissolved in water. Add 100 milliliters of 1:1 sulphuric acid, dilute with water in a 1,000 milliliter volumetric flask and shake evenly.

Determination of the ammonium ferrous sulphate standard solution: put 10 milliliters of 0.1N potassium dichromate standard solution in a 250 milliliter Erlenmeyer flask, add 10 milliliters of 1:1 sulphuric acid, 100 milliliters of water, drip in 3 drops of phenyl substituted amino benzoic acid and titrate with ammonium ferrous sulphate solution until the solution changes from purple to green.

The equivalent concentration (N) of the ammonium ferrous sulphate standard solution is calculated by the following formula:

$$N = \frac{N_1 V_1}{V}$$

In the formula:  $N_1$  is the equivalent concentration of the potassium dichromate standard solution;  $V_1$  is the volume (milliliters) of the potassium dichromate;  $V$  is the volume (milliliters) of ammonium ferrous sulphate consumed during titration.



### 3. Analysis Procedure

A 0.5 gram sample is placed in a 250 milliliter Erlenmeyer flask, add 20 milliliters of 1:1 sulphuric acid, heat and dissolve. After dissolving, drip in nitric acid and oxidize until the solution's purple color disappears. Continue evaporation until the sulphuric acid emits smoke, cool and dilute with water to 100 milliliters. Drip in a 10% potassium permanganate solution and oxidize until the solution has a stable pink color. Lay aside for three minutes, then add 1.5 grams of urea, and drip in a 1% sodium nitrate solution until the pink color totally disappears. Lay still for three minutes, then drip in three drops of phenyl substituted amino benzoic acid indicator and titrate with an ammonium ferrous sulphate normal solution until the solution changes from purple to green.

### 4. Calculations

The percentage content of vanadium is calculated by the following formula:

$$V\% = \frac{NV \times 50.95}{G \times 1,000} \times 100$$

In the formula, N is the equivalent density of the ammonium ferrous sulphate standard solution; V is the volume (milliliters) of the ammonium ferrous sulphate during titration; 50.95 is the vanadium's gram equivalent; G is the sample's weight (grams).

### 5. Allowable Deviation

Vanadium Content %

1 - 5  
5 - 10

Allowable Deviation %

± 0.05  
± 0.10

Note: Because the indicator, a phenyl substituted amino benzoic acid solution, has reductivity, a small amount should be used and the amount used during determination and analysis should be the same.

## II. The Tantalum Reagent - Trichloromethane Extraction Absorption Luminosity Method

### 1. Summary of Method

In a sulphuric acid medium, four valence titanium is oxidized to five valence by potassium permanganate. When there is urea, the excessive amount of potassium permanganate is reduced by sodium nitrate. The five valence vanadium and tantalum reagents produce a phenyl color complex compound which is extracted by the trichloromethane. The vanadium content is measured according to the depth of color.

Determination range: 0.50-1.00%.

### 2. Reagent

Sulphuric acid: 1:1  
Nitric acid : specific weight 1.42  
Potassium permanganate: 1% solution  
Urea : 20% solution  
Sodium nitrate: 1% solution

Tantalum reagent: a 0.2% trichloromethane-alcohol solution. One gram of tantalum reagent (benzoylphenyl carbonol amine) is dissolved in a mixture of 100 milliliters of alcohol and 400 milliliters of trichloromethane and shaken evenly (new composition).

Vanadium standard solution: 0.2296 grams of spectrum pure

amino vanadate are dissolved in water (or diluted sulphuric acid), transferred into a 1,000 milliliter volumetric flask, diluted to calibration by water and shaken evenly.

50 milliliters of the above mentioned solution are separated and put into a 250 milliliter volumetric flask, water is used to dilute to calibration and it is shaken evenly. Each milliliter of this solution contains 0.02 milligrams of vanadium.

### 3. Analysis Procedure

Place a 0.1 gram sample into a 100 milliliter beaker and add 10 milliliters of 1:1 sulphuric acid. After heating and diluting, drip in nitric acid and oxidize until the purple of the solution disappears. Continue heating and evaporate until the sulphuric acid emits smoke, and then cool. Use a small amount of water to wash the surface plate and beaker wall. Then evaporate until the sulphuric acid emits smoke and cool. Transfer into a 100 milliliter volumetric flask, dilute with water until calibration and shake evenly.

Separate out 10 milliliters of the above solution and place it in a 125 milliliter separatory funnel. Add 15 milliliters of water and drip in a 1% potassium permanganate solution under constant shaking until the solution has a light red color. Put aside for 1-2 minutes. Add 2 milliliters of 20% urea and while shaking add a 1% sodium nitrite solution until the solution's light red color disappears. Then add precisely four drops into 20 milliliters of the tantalum reagent and shake

for 2 minutes. After placing the separate layers, a small quantity of absorbent cotton is stuffed in the lower opening of the separatory funnel. The organic phase is filtered in a dried one centimeter colorimetric dish. Measure the absorption luminosity in a 470-480 millimicrometer wavelength and find the vanadium content on the standard curve.

Reference solution: the same as the reference solution of the standard curve.

#### 4. Calculations

The percentage content of vanadium is calculated by the following formula:

$$V\% = \frac{G_1}{G} \times 100$$

In the formula,  $G_1$  is the weight (milligrams) of the vanadium found on the standard curve;  $G$  is the weight (milligrams) of the specimen contained in the developing solution.

#### 5. Drawing of the Standard Curve

Take 0.1 grams of sponge titanium or a titanium alloy without vanadium and after dissolving by the analysis procedure, transfer into a 100 milliliter volumetric flask, dilute with water until calibration and shake evenly.

Divide the above solution into several parts and place in a 125 milliliter separatory funnel and separately add in 0, 2.0, 4.0, 6.0, 8.0 and 10.0 milliliters of vanadium standard solution. With constant shaking, drip in a 1% potassium manganate solution until the solution is light red. Carry out according

to the analysis procedure. Use a reagent blank as the reference solution to measure the absorption luminosity and draw the standard curve.

6. Allowable Deviation

Vanadium Content %

0.5 - 1.0

Allowable Deviation %

$\pm 0.05$

STANDARD FOR THE DETERMINATION OF  
MOLYBDENUM IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

I. The Sulfocyanate Absorption Luminosity Method

1. Summary of Method

When there are iron ions in a sulphuric acid medium, ascorbic acid is used as the reducing agent to reduce the six valence molybdenum to five valence. The five valence molybdenum and sulfocyanate produce an orange-red colored complex. The molybdenum content is determined according to the depth of the color.

Determination range: 0.50-9.00%.

1. Reagent

Sulphuric acid	: 1:1
Nitric acid	: specific weight 1.42
Ascorbic acid	: 10% solution
Sodium thiocyanate	: 50% solution

Ferrous sulphate: place 0.5 grams of pure iron into a 200 milliliter beaker, add 20 milliliters of 1:1 sulphuric acid and heat and dissolve. Drip in nitric acid for oxidation and continually heat and evaporate until the sulphuric acid emits smoke. Drive out the nitric acid and cool. Add in a small amount of water and transfer to a 500 milliliter volumetric flask. Dilute with water until calibration and shake evenly. Each

milliliter of this solution contains 1 milligram of iron.

Molybdenum standard solution: place 0.1 grams of pure molybdenum in a 250 milliliter beaker, add 10 milliliters of <sup>1:1</sup> sulphuric acid and 10 milliliters of nitric acid, heat and dissolve. Continually heat and evaporate until sulphuric acid emits smoke for 2-3 minutes. Eliminate the nitric acid and cool. Add in a small amount of water and transfer into a 1,000 milliliter volumetric flask. Dilute with water until calibration and shake evenly. Each milliliter of solution contains 0.1 milligrams of molybdenum.

### 3. Analysis Procedure

Place a 0.1 gram sample into a 150 milliliter beaker, add 10 milliliters of 1:1 sulphuric acid and after heating and dissolving, drip in nitric acid and oxidize until the solution's purple color disappears. Continually heat and evaporate until the sulphuric acid emits smoke, cool and transfer into a 100 milliliter volumetric flask. Dilute with water until calibration and shake evenly.

Put 10 milliliters of the above solution in a 100 milliliter volumetric flask, add 15 milliliters of <sup>1:1</sup> sulphuric acid and 25 milliliters of water and shake evenly. Add a 1 milliliter ferrous sulphate solution, 7 milliliter of a 50% thiocyanic acid solution, 10 milliliters of a 10% ascorbic acid solution, dilute with water until calibration and shake evenly. After placing it aside for 15 minutes, use a one centimeter colorimetric dish to measure the light absorption in an area with a 470 millimicrometer wavelength and find the molybdenum content

on the standard curve.

Reference liquid content: Same as the reference liquid content for the standard curve.

#### 4. Calculations

The percentage content of molybdenum is calculated by the following formula:

$$\text{Mo\%} = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the molybdenum found on the standard curve;  $G$  is the weight (milligrams) of the sample contained in the developing solution.

#### 5. Drawing of the Standard Curve

Separately add 0,10,20,30,40,50 and 60 milliliter of molybdenum standard solution into several 100 milliliter volumetric flasks, and add 15 milliliters of 1:1 sulphuric acid, 25 milliliters of water, 1 milliliter of ferrous sulphate solution, 7 milliliters of a 50% sodium thiocyanate solution and 10 milliliters of 10% ascorbic acid, then shake evenly. The following is carried out according to the analysis procedure. Measure the absorption luminosity and draw the standard curve.

#### 6. Allowable Deviation

Molybdenum Content %	Allowable Deviation %
0.5 - 1.0	$\pm 0.05$
1.0 - 5.0	$\pm 0.10$
5.0 - 9.0	$\pm 0.15$

Note: When the molybdenum quantity in the sample is greater than 5%, separate out 5 milliliters of the solution according to the analysis procedure.

## II. A - Benzoin Oxime Weight Method



### 1. Summary of Method

In a cold acid solution, the molybdenum and A - benzoin oxime form a non-soluble complex. After filtering and burning the non-pure molybdenum trioxide is weighed. Ammonia water is used to dissolve the molybdenum trioxide and after filtering and burning the mixed oxide is weighed again. Based on the difference between the two weighings we calculate the percentage content of molybdenum in the sample.

The disturbance of the vanadium and chromium is eliminated by ferrite reduction.

Determination range: 0.50-9.00%.

### 2. Reagent

Sulphuric acid: specific weight 1.84, 1:1

Nitric acid : specific weight 1.42

Bromine water : saturated bromine water

Ammonium ferrosulphate: 10% solution. Dissolve 50 grams of ammonium ferrosulphate into 250 milliliters of water, add 50 milliliters of 1:1 sulphuric acid and cool. Dilute with water until 500 milliliters and shake evenly.

A - benzoin oxime: 2% alcohol solution.

A - benzoin oxime washing solution: take 10 milliliters of A - benzoin oxime solution, add 10 milliliters of 1:1 sulphuric acid, dilute with water until 500 milliliters and shake evenly. Place in cold water before using to decrease the temperature.

Ammonia water: specific weight 0.90.

### 3. Analysis Procedure

Place a 0.5 - 1.0 gram sample (containing 30-40 milligrams

of molybdenum) in a 300 milliliter beaker, add 30 milliliters of 1:1 sulphuric acid, heat at a low temperature until the sample is completely dissolved and drip in nitric acid and oxidize until the solution's purple color disappears. Continually heat until the sulphuric acid emits smoke, then cool. Dilute with water until about 100 milliliters and cool to under  $10^{\circ}\text{C}$  in cold water (for a sample with vanadium and chromium add 5 milliliters of ammonium ferrosulphate). With constant shaking, add in 20-25 milliliters of a 2% A - benzoin oxime solution (5 milliliters should be added in for each 10 milligrams of molybdenum so that there is finally an excess of 5 milliliters), constantly shake and add 5 milliliters of saturated bromine water until there is a dull yellow color. Then add 5 milliliters of a 2% A - benzoin oxime solution, shake for a short while and after 15 minutes filter with mid-speed filter paper. Use A - benzoin oxime to wash the washing solution beaker two to three times, use a small piece of filter paper to rub off the sediment on the beaker wall and rinse in the funnel. Rinse the sediment about ten to twelve times and put the sediment and filter paper in the original platinum crucible. Place in an oven and bake until the filter paper turns yellow. Afterwards, transfer it into a high temperature furnace and raise the temperature to  $500^{\circ}\text{C}$ . Bake for 90-120 minutes, cool to room temperature and weigh  $G_1$ . Add 25 milliliters of ammonia water into the platinum crucible. Heat until the molybdenum trioxide is completely dissolved and filter with

mid-speed filter paper. Further, use a 1:99 hot ammonia water solution to rinse eight to ten times. Then use warm water to rinse three to four times. Transfer the sediment and filter paper into the original platinum crucible, dry and ash, then transfer into a high temperature furnace and burn for 30 minutes at 300°C. Cool to room temperature and weigh  $G_2$ .

#### 4. Calculations

The percentage content of molybdenum is calculated by the following formula:

$$\text{Mo\%} = \frac{(G_1 - G_2) \times 0.667}{G} \times 100$$

In the formula:  $G_1$  is the weight (grams) of the molybdenum trioxide and platinum crucible;  $G_2$  is the weight (grams) of the residue and platinum crucible;  $G$  is the weight (grams) of the sample; 0.667 is the coefficient of the molybdenum trioxide converted into molybdenum.

#### 5. Allowable Deviation

Molybdenum Content %	Allowable Deviation %
0.5 - 1.0	$\pm 0.05$
1.0 - 5.0	$\pm 0.10$
5.0 - 9.0	$\pm 0.15$

## STANDARD FOR THE DETERMINATION OF TIN IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

### The Potassium Iodate Volumetric Method

#### 1. Summary of Method

In an acid medium with the protection of carbon dioxide gas, we can reduce four valence tin to two valence with aluminum plate or iron powder. We take amylum as the indicator and use a potassium iodate standard solution for titration. The tin content is converted according to the amount of potassium iodate standard solution consumed.

Titanium, aluminum etc. do not interfere with determination but there is interference with vanadium, copper, molybdenum and oxidizing agents. Samples with relatively high contents of vanadium, copper and molybdenum must separate the tin sediment and titanium, copper, vanadium and molybdenum by ammonia water in hydrogen peroxide after being dissolved in sulphuric acid. After the sediment is dissolved by hydrochloric acid, we use the iodate volumetric method to determine the tin.

Determination range: above 0.5%.

#### 2. Reagent

Hydrochloric acid: 1:1; 5%  
Sulphuric acid : 1:1  
Hydrogen peroxide: 30%

Fluoboric acid : 40%.  
Ammonia water : specific weight 0.90: 1:1.  
Sodium bicarbonate: saturated solution  
Reduced iron powder or aluminum plate: over 99.9%  
Amylum indicator : 0.5% solution (newly made)  
Scouring agent : dissolve 25 grams of ammonium chloride  
in 500 milliliters of water, add 10  
milliliters of hydrogen peroxide and  
dilute with ammonia water to pH=8-9.

Tin standard solution: place 1 gram of pure tin in a 250 milliliter beaker, use 100 milliliters of 1:1 sulphuric acid to heat and dissolve at a low temperature and cool. Transfer into a 1,000 milliliter volumetric flask, dilute with water until calibration and shake evenly. Each milliliter of this solution contains 1 milligram of tin.

Potassium iodate solution: 0.02N. Dissolve 0.7134 grams of potassium iodate and 10 grams of potassium iodide in water, add 25 milliliters of 0.05N sodium hydroxide and transfer into a 1,000 milliliter volumetric flask. Dilute with water until calibration and shake evenly.

The following method is used to determine the titration degree of the potassium iodate standard solution on tin:

(A) Place 0.2 grams of pure titanium in a 500 milliliter Erlenmeyer flask, add 10 milliliters of tin standard solution and 10 milliliters of 1:1 sulphuric acid, heat and dissolve and carry out the following according to analysis procedure A (suitable for calculating analysis procedure A).

(B) Place 10 milliliters of tin standard solution in a 500 milliliter Erlenmeyer flask, add 40 milliliters of concentrated hydrochloric acid, 80 milliliters of water, 5 milliliters

of fluoboride, 2-3 grams of iron powder or aluminum plate, and carry out the following according to analysis procedure B (suitable for calculating analysis procedure B).

The titration of potassium iodide standard solution on tin is expressed by T and calculated by the following formula:

$$T = \frac{g}{V}$$

In the formula: g is the weight (milligrams) of the tin contained in the tin standard solution; V is the volume (milliliters) of potassium iodide standard solution consumed by titration.

### 3. Analysis Procedure

(A) Place a 0.2 gram sample in a 500 milliliter Erlenmeyer flask, add 10 milliliters of sulphuric acid, 5 milliliters of 40% fluoboride, 80 milliliters of water, 40 milliliters of hydrochloric acid and 2-3 grams of iron powder. Cover the Geissler funnel with saturated sodium hydrocarbide solution and heat at a low temperature. After waiting until the iron powder completely dissolves, heat again to a boil until the solution has air bubbles. Take down, cool to room temperature with flowing water and carefully pour the saturated sodium hydrocarbide in the funnel into an Erlenmeyer flask. Immediately add 10 milliliters of 0.5% amylum indicator, titrate with a potassium iodide standard solution until there is a stable blue color.

(B) Put a 0.2 gram sample in a 500 milliliter beaker, add 10 milliliters of 1:1 sulphuric acid, heat and dissolve.

Continuously drip in 30% hydrogen peroxide and after the sample is completely dissolved, cool. Clean the beaker with water, add 25 milliliters of 30% hydrogen peroxide, 150 milliliters of water and titrate to pH 8-9 with 1:1 ammonium hydroxide. Set aside for ten minutes and then use fast speed filter paper to wash 3-4 times. Use 100 milliliters of hot 1:1 hydrochloric acid to dissolve the sediment and filter paper in the original beaker. Then use a hot 5% hydrochloric acid solution to clean the funnel, pour the solution into an Erlenmeyer flask (total volume should not exceed 200 milliliters), add 5 milliliters of fluoboric acid, 2-3 grams of reduced iron powder, cover the Geissler funnel with a saturated sodium hydrocarbide and heat at a low temperature until the iron powder is completely dissolved. Then, heat and boil until the solution shows large bubbles, cool with water to room temperature and carefully pour the sodium hydrocarbide solution in the funnel into the Erlenmeyer flask. Immediately add 10 milliliters of 0.5% amylum indicator and titrate with a potassium iodide standard solution until there is a stable blue color.

#### 4. Calculations

The percentage content of tin is calculated by the following formula:

$$\text{Sn\%} = \frac{T \cdot V}{G} \times 100$$

In the formula: T is the titration (milligrams/milliliter) of the potassium iodide solution on tin; V is the volume (milliliters) of potassium iodide standard solution consumed

during titration; G is the sample's weight (milligrams).

#### 5. Allowable Deviation

Tin Content %	Allowable Deviation %
2 - 5	$\pm 0.10$
5 - 10	$\pm 0.15$

#### Notes:

(1) Carried out in most situations according to analysis procedure A and when the sample contains vanadium, molybdenum (over 5%) and copper (over 1%) it is necessary to use analysis procedure B.

(2) When using analysis procedure B, it is necessary to add 25 milliliters of 30% hydrogen peroxide after cooling, otherwise the hydrogen peroxide dissolves. Further, the use of ammonium hydroxide titrated to pH=8-9 causes the sediment to separate out, otherwise the sediment condition will be poor and it will not be easy to filter.

(3) When using procedure A, the hydrogen peroxide must be completely eliminated because the oxidizer affects the determination of tin.

(4) Prior to titration, a sufficient quantity of saturated sodium hydrocarbide solution must be maintained in the Geissler funnel to guarantee the reduction of the tin under the protection of the carbon dioxide gas, otherwise air can enter into the Erlenmeyer flask, oxidize the tin and cause the results to be lower.

(5) If we add aluminum plate to reduce the tin, we should first wait for the reaction to slow down in room temperature



and then heat at a low temperature completely dissolving the aluminum plate.

(6) When we do not have a Geissler funnel, we use a rubber stopper with an air vent tube to stop up the Erlenmeyer flask. The other end of the air vent tube enters into the 150 milliliter beaker with saturated sodium hydrocarbide solution.

(7) When method B is used to separate the sediment, if there is no aluminum in the sample, we must add 10 milligrams of aluminum for precipitation otherwise the results will not be stable.

STANDARD FOR THE DETERMINATION  
OF ZIRCONIUM IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

I. The Bitter Almond Acid Weight Method

1. Summary of Method

In a hydrochloric acid medium, zirconium and bitter almond acid produce white zirconium bitter almond acid.

[ $\text{ZrC}_3\text{H}_7\text{O}_3$ ] sediment. Filter, burn to produce zirconium dioxide and weigh. Melt with coking potassium sulfate and use the hydrogen peroxide absorption luminosity method to determine the mixed titanium dioxide quantity. After being deducted from the total weight, calculate the zirconium content in the sample. The sulphuric acid root ions, fluorine ions and tartaric acid root ions influence the production of sediment and cause the results to be lower.

Determination range: 0.50 - 5.00%.

Hydrochloric acid : specific weight 1.19  
Bitter almond acid: 15% solution (used after filtering)  
Coking potassium sulfate: solid  
Hydrogen peroxide : 30%

Titanium dioxide standard solution: place 0.5995 grams of pure titanium in a 250 milliliter beaker, add 40 milliliters of 1:1 sulphuric acid and after heating and dissolving drip in nitric acid to oxidize until the solution's purple color disappears. Continuously heat and evaporate until the sulphuric

acid emits smoke, cool and transfer into a 1,000 milliliter volumetric flask. Dilute with water until calibration and shake evenly. Each milliliter of this solution contains one milligram of titanium dioxide.

Bitter almond acid washing solution: add 50 milliliters of bitter almond acid solution in 500 milliliters of 2% hydrochloric acid.

### 3. Analysis Procedure

Place a 0.5-1.0 gram sample in a 300 milliliter beaker, add 60 milliliters of hydrochloric acid and heat and dissolve at a low temperature in a sand bath. After it is dissolved, add 50 milliliters of water and filter the solution with fast speed filter paper into a 400 milliliter beaker. Use 5% hydrochloric acid to rinse the beaker and filter paper eight times. Heat the filtered solution (total volume is about 200 milliliters) until near boiling, add 50 milliliters of a 15% bitter almond acid solution while shaking and continue to shake until the sediment is separated out. Place in a hot water bath (80-90°C) and maintain temperature for 40 minutes. Slow speed filter paper is used to filter the solution with sediment and the bitter almond acid washing solution is used to wash the sediment 8-10 times. The sediment and filter paper are placed in a constant weight platinum crucible (or porcelain crucible) and after ashing transferred into a high temperature furnace to be burned for one hour at 1,000°C. It is placed in a dryer, cooled to room temperature and then we obtain weight  $G_1$  (grams).

Add 4 grams of coking potassium sulfate into the crucible, place in a high temperature furnace and melt for three minutes at 800°C. Take out to cool and place in a 300 milliliter beaker. Add 50 milliliters of water, heat and obtain a fused piece. Transfer the solution into a 100 milliliter volumetric flask and after cooling add 10 milliliters of 1:1 sulphuric acid and two drops of 30% hydrogen peroxide. Dilute with water until calibration and shake evenly. Use a 2 centimeter colorimetric dish in a 420 millimicrometer wavelength area to measure the absorption luminosity. Find weight  $G_2$  (grams) of the titanium dioxide on the titanium dioxide standard curve.

#### 4. Calculations

The percentage content of zirconium is calculated by the following formula:

$$\text{Zr\%} = \frac{(G_1 - G_2) \times 0.7403}{G} \times 100$$

In the formula:  $G_1$  is the weight (grams) of the zirconium oxide and titanium dioxide;  $G_2$  is the weight (grams) of the titanium dioxide; 0.7403 is the coefficient of the zirconium oxide converted into zirconium;  $G$  is the sample's weight (grams).

#### 5. Drawing the Titanium Dioxide Standard Curve

0.0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 milliliter titanium dioxide standard solutions are separately added into several 100 milliliter volumetric flasks. Add 10 millimeters of 1:1 sulphuric acid, add water up to about 50-60 milliliters, add two drops of 30% hydrogen peroxide, dilute with water until calibration and shake evenly. Use a 2 centimeter colorimetric dish in a 420

millimicrometer wavelength area to measure the absorption luminosity and draw the standard curve.

#### 6. Allowable Deviation

Zirconium Content %	Allowable Deviation %
0.5 - 1.50	$\pm 0.04$
1.50 - 3.00	$\pm 0.06$
3.00 - 5.00	$\pm 0.08$

## II. The EDTA Volumetric Method

### 1. Summary of Method

In a 1-1.2N hydrochloric acid solution with dimethyl phenol orange as the indicator, we use an EDTA standard solution to titrate the zirconium until the solution suddenly changes from red to yellow. We convert the content of zirconium based on the consumption of the EDTA standard solution.

Determination range: 0.50 - 5.00%.

### 2. Reagent

Hydrochloric acid : specific weight 1.19: 1:1  
Nitric acid : specific weight 1.42  
Dimethyl phenol orange: 0.5% solution  
Hydroxylamine hydrochloride: solid

Zirconium standard solution: place 3.606 grams of zirconium chloride into a 250 milliliter beaker, dissolve with 200 milliliters of 1:1 hydrochloric acid, transfer into a 1,000 milliliter volumetric flask, dilute with water until calibration and shake evenly. Each milliliter of this solution contains one milligram of zirconium. The bitter almond acid weight method is used for calibration.

Calibration method: put 50 milliliters of zirconium standard

solution into a 400 milliliter beaker and dilute with water to 100 milliliters. Add 40 milliliters of hydrochloric acid and 50 milliliters of a 16% bitter almond acid solution, heat to about 85°C and shake thoroughly. Put aside for over 4 hours, filter and wash 7-8 times with a hot washing solution (2 grams of bitter almond acid are dissolved in 100 milliliters of 2% hydrochloric acid). The sediment and filter paper are placed in a porcelain crucible and ashed. It is transferred into a high temperature furnace and baked for one hour at 1,000°C. It is taken out and cooled and placed in a dryer, then weighed after cooling to room temperature. The coefficient of the zirconium dioxide converting into zirconium is 0.7403.

EDTA standard solution: 0.005M. Dissolve 3.72 grams of EDTA disodium salt in warm water and transfer into a 2,000 milliliter volumetric flask after cooling. Dilute with water until calibration and shake evenly.

EDTA standard solution's determination of zirconium titration: take 10 milliliters of zirconium standard solution, add 30 milliliters of 1:1 hydrochloric acid and dilute with water to 150 milliliters. Carry out by the analysis procedure. Titration T is calculated by the following formula:

$$T = \frac{g}{v}$$

In the formula: g is the weight (milligrams) of zirconium contained in 10 milliliters of zirconium standard solution; v is the volume (milliliters) of consumed EDTA solution during titration.

### 3. Analysis Procedure

Place a 0.2 - 0.5 gram sample in a 500 milliliter Erlenmeyer flask, add 30 milliliters of concentrated hydrochloric acid and cover the surface dish. Heat and dissolve in a sand bath or low temperature electric furnace and after the sample is completely dissolved add several drops of nitric acid for oxidation. Boil to eliminate the nitrogen oxide (at this time, the volume is about 30 milliliters), and if there is not 30 milliliters use 1:1 hydrochloric acid to compensate and make up the 30 milliliters. Cool slightly, dilute with water until 200 milliliters, heat and boil for a short time, take down and immediately add 0.5 grams of hydroxylamine hydrochloride. Then add 2 drops of 0.5% dimethyl phenol orange solution and titrate with 0.005 MEDTA standard solution into a bright yellow color. Boil the solution until it does not turn red.

### 4. Calculations

The percentage content of zirconium is calculated by the following formula:

$$\text{Zr\%} = \frac{V \cdot T}{G} \times 100$$

In the formula: T is the titration (milligrams/milliliter) of the EDTA standard solution on zirconium; V is the volume (milliliters) of EDTA standard solution consumed during titration; G is the sample's weight (milligrams).

### 5. Allowable Deviation

Zirconium Content %	Allowable Deviation %
0.5 - 1.5	$\pm 0.06$
1.5 - 3.0	$\pm 0.08$
3.0 - 5.0	$\pm 0.10$

Notes:

(1) It is best that the acidity of the solution be 1-1.2N during titration. If the acidity is lower or higher than this, the final point will not be easy to discriminate during titration.

(2) If the sample contains chromium, we can add 2 more drops of indicator.

(3) When dissolving the sample, the mouth of the Erlenmeyer flask should be covered with a surface plate and low temperature heating is used for dissolving.



STANDARD FOR THE DETERMINATION  
OF IRON IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

The Ortho-Phenanthroline Absorption Luminosity Method

1. Summary of Method

In a sulphuric acid medium, citric acid is used for complexing titanium and other elements. In a slight acid solution, two valence iron ions and ortho-phenanthroline produce a red colored complex. We determine the iron content by the darkness of the color.

Determination range: 0.01 - 2.0%.

2. Reagent

Sulphuric acid: 1:1  
Nitric acid : specific weight 1.42  
Citric acid : 50% solution  
Hydroxylamine hydrochloride: 10% solution  
Ortho-phenanthroline : 0.3% solution

Iron standard solution: take 0.1 gram of pure iron and add 30 milliliters of concentrated hydrochloric acid. After heating and dissolving, cool and transfer into a 1,000 milliliter volumetric flask. Dilute with water until calibration and shake evenly. Each milliliter of this solution contains 0.1 milligrams of iron.

3. Analysis Procedure

Place a 0.1 gram sample in a 150 milliliter beaker, add 10

milliliters of 1:1 sulphuric acid and heat until the sample is dissolved. Drip in nitric acid and oxidize until the solution's purple color disappears. Continue to evaporate until the sulphuric acid emits smoke. Take down to cool and transfer into a 100 milliliter volumetric flask. Dilute with water until calibration and shake evenly.

Separate 10 milliliters of the solution into a 100 milliliter volumetric flask, add 10 milliliters of a 50% citric acid solution, 5 milliliters of a 10% hydroxylamine hydrochloride solution, put in a small piece of Congo red test paper and drip in 1:1 ammonia water and dilute until the Congo red test paper assumes a purplish red color. Heat until near boiling, take down, add in 10 milliliters of 0.3% ortho-phenanthroline solution and cool. Dilute with water until calibration and shake evenly.

Use a 3 centimeter colorimetric dish to measure the absorption luminosity in a 510 millimicrometer wavelength area and then find the iron content from the standard curve.

Reference solution: identical to the reference solution of the standard curve.

#### 4. Calculations

The percentage content of iron is calculated by the following formula:

$$\text{Fe\%} = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the iron

found on the standard curve; G is the sample's weight (milligrams) contained in the color solution.

#### 5. Drawing of the Standard Curve

Separately add 0,1.0,2.0,4.0,6.0,8.0 and 10.0 milliliters of iron standard solution into several 100 millileter volumetric flasks. Add 10 milliliters of a 50% citric acid solution and 5 milliliters of a 10% hydroxylamine hydrochloride, ..... carry out the following according to the analysis procedure, measure the absorption luminosity and draw the standard curve.

#### 6. Allowable Deviation

Iron Content %	Allowable Deviation %
0.01 - 0.10	$\pm 0.005$
0.10 - 0.50	$\pm 0.02$
0.50 - 2.0	$\pm 0.05$

#### Notes:

(1) When containing 0.01-0.1% iron, we can use the whole sample solution to show color; when containing 0.1-1.0% iron, we can use one-tenth of the sample to show color; when containing 1.0-2.0% iron, we can use 5% of the sample to show color.

(2) When the iron content is less than 0.05%, we must use double distilled water.

STANDARD FOR THE DETERMINATION  
OF SILICON IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

The Molybdenum Blue Colorimetric Method

1. Summary of Method

In a diluted sulphuric acid medium, silicon and ammonium molybdate produce many yellow acids and a large quantity of titanium blocks the molybdenum from issuing color. Yet, adding an excessive amount of ammonium molybdate causes titanium to become titanium molybdate sediment and normally issues color. After issuing color, the acidity is increased causing the titanium molybdate sediment to dissolve. Ascorbic acid is used to reduce the silicon into molybdenum blue. The silicon content is determined by the depth of the color.

Determination range: 0.02 - 0.50%.

2. Reagent

Sulphuric acid	: 1:3
Hydrofluoric acid	: 40%
Boric acid	: saturated solution
Potassium permanganate	: 4% solution
Ammonium molybdate	: 20% solution
Ascorbic acid	: 4% solution

Silicon standard solution: place 12.12 grams of sodium silicate in a 500 milliliter beaker, add 300 milliliters of water and 40 milliliters of a 4% sodium hydroxide solution. After

shaking evenly, heat and boil for several minutes, cool to room temperature and filter into a 1,000 milliliter volumetric flask. Dilute with water until calibration and shake evenly. Store in a plastic container. Each milliliter of this solution contains about 1 milligram of silicon.

Separate and place 10 milliliters of the above solution in a 1,000 milliliter volumetric flask, dilute with water until calibration and shake evenly. Store in a plastic container. Each milliliter of this solution contains about 0.01 milligrams of silicon.

Calibration of the silicon standard solution:

Separate 50 milliliters of silicon standard solution (1 milliliter contains about 1 milligram of silicon) and use the weight method for the double dehydration calibration of sulphuric acid.

### 3. Analysis Procedure

Place a 0.1 - 0.2 gram sample in a 250 milliliter plastic beaker, add 20 milliliters of 1:3 sulphuric acid and 10 drops of hydrofluoric acid. Put a cover on and lay aside at room temperature to dissolve. After the sample dissolves, add 20 milliliters of saturated boric acid and drip in a 4% potassium permanganate solution until the solution has a stable red color. Transfer into a 100 milliliter volumetric flask, dilute with water until calibration and shake evenly. Immediately transfer into a 250 milliliter plastic beaker.

Separate and place 10 milliliters of the test solution in

a 250 milliliter plastic beaker, add 30 milliliters of water (at this time, the temperature of the solution is controlled between 20°C-25°C). Add 10 milliliters of a 20% ammonium molybdate solution, set aside for 20 minutes, add 20 milliliters of 1:3 sulphuric acid, shake evenly, add 2 milliliters of a 4% ascorbic acid solution, shake evenly and set aside for 20 minutes. Transfer to a 100 milliliter volumetric flask, dilute with water until calibration and shake evenly. Use a 2 centimeter colorimetric dish to measure the absorption luminosity in a 700 millimicrometer wavelength area and find the silicon content from the standard curve.

#### 4. Calculations

The percentage content of silicon is calculated by the following formula:

$$\text{Si}\% = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the silicon found from the standard curve;  $G$  is the weight (milligrams) of the sample contained in the color solution.

#### 5. Drawing of the Standard Curve

Add 0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 milliliters of silicon standard solution into several plastic beakers, add 1 drop of hydrofluoride, 2 milliliters of saturated boric acid, 2 milliliters of 1:3 sulphuric acid and 1 drop of a 4% potassium permanganate solution. Dilute with water until the volume is about 40 milliliters, add 10 milliliters of a 20% ammonium molybdate solution and set aside for 20 minutes. Add 20 milliliters

of 1:3 sulphuric acid and 2 milliliters of a 4% ascorbic acid solution, shake evenly and set aside for 20 minutes. Transfer to a 100 milliliter volumetric flask, dilute with water until calibration and shake evenly. Use a 2 centimeter colorimetric dish to measure the light absorbancy in a 700 millimicrometer wavelength area and draw the standard curve.

Reference solution: reagent blank.

#### 6. Allowable Deviation

Silicon Content %	Allowable Deviation %
0.02 - 0.10	$\pm 0.005$
0.10 - 0.50	$\pm 0.02$

#### Notes:

(1) The molybdenum blue method of determining silicon requires very stringent operation. The reagents used must be first grade. The water must be distilled; ionized water should not be used.

(2) During the developing color process, each time a reagent is added, we should clean the beaker wall with water and shake evenly, otherwise the results will be unstable.

(3) The production of molybdenum yellow is related to temperature and therefore it is best for the temperature to be controlled between 20°C-25°C.

(4) Tests prove that the maximum absorption peak of molybdenum blue is in the 760 millimicrometer area. Yet, the presently often used type 72 spectrometer cannot attain this wavelength. When we consider the broadness of application, this test consistently used a 700 millimicrometer wavelength.

(5) When the silicon content is greater than 0.5%, we use a 1 centimeter colorimetric dish.



STANDARD FOR THE DETERMINATION OF  
MANGANESE IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

I. The Potassium Periodate Absorption Luminosity Method

1. Summary of Method

In a sulphuric acid medium, potassium periodate is used to oxidize two valence manganese into a purplish red permanganate. The manganese content is determined by the depth of the color.

Determination range: 0.5 - 3.0%.

2. Reagent

Sulphuric acid : 1:1  
Nitric acid : specific weight 1.42  
Potassium periodate: solid  
EDTA : 5% solution

Manganese standard solution: place 0.1 grams of pure manganese in a 200 milliliter beaker, add 20 milliliters of 1:4 sulphuric acid, 2 milliliters of nitric acid, heat and dissolve. Evaporate until the sulphuric acid emits smoke, then cool. Add 50 milliliters of water, heat and dissolve the salt, then cool. Transfer into a 1,000 milliliter volumetric flask, dilute with water until calibration and shake evenly. Each milliliter of this solution contains 0.1 milligrams of manganese.

3. Analysis Procedure

Place a 0.1 gram sample in a 100 milliliter beaker and

add 10 milliliters of 1:1 sulphuric acid. After heating and dissolving, drip in nitric acid and oxidize until the solution's purple color disappears. Continue to evaporate until the sulphuric acid emits smoke and then cool. Transfer into a 100 milliliter volumetric flask, dilute with water until calibration and shake evenly.

Separate out 10 milliliters of the above solution and put it in a 100 milliliter beaker. Add 10 milliliters of water, 5 milliliters of 1:1 sulphuric acid and 0.5 grams of potassium periodate. Heat and boil until the manganese completely oxidizes and then cool. Transfer into a 100 milliliter volumetric flask, dilute with water until calibration and shake evenly. Use a 3 centimeter colorimetric dish to measure the absorption luminosity in a 530 millimicrometer wavelength area and find the manganese content on the standard curve.

Reference solution: after pouring out part of the color solution, add 20 drops of a 5% EDTA solution to the remaining solution in the volumetric flask and shake evenly. After the red color disappears it acts as the reference solution.

#### 4. Calculations

The percentage content of manganese is calculated by the following formula:

$$\text{Mn\%} = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the manganese found in the standard curve;  $G$  is the weight (milligrams) of

the sample contained in the color solution.

#### 5. Drawing of the Standard Curve

Separately add 0, 0.5, 1.0, 2.0, 3.0 and 4.0 milliliters of manganese standard solution in several 100 milliliter beakers. Dilute with water to 15 milliliters, carry out according to the analysis procedure, measure the absorption luminosity and draw the standard curve.

#### 6. Allowable Deviation

Manganese Content %	Allowable Deviation %
0.5 - 1.5	$\pm 0.02$
1.5 - 3.0	$\pm 0.05$

#### Notes:

- (1) When showing color, the acidity is not lower than 10%.
- (2) When showing color, the temperature should not be too high otherwise oxidation will be incomplete.

## II. The Arsinic Acid - Nitrite Volumetric Method

### 1. Summary of Method

In a sulphuric acid solution, we use silver nitrate as the catalyst. Ammonium persulfate is used to oxidize the manganese into seven valence permanganate and a arsinic acid - sodium nitrite standard solution is used for titration until the purplish red color disappears.

Determination range: 0.1 - 2%.

### 2. Reagent

Sulphuric acid : 1:1; 2:3  
Hydrofluoric acid: 40%

Silver nitrate : 1% solution  
Ammonium persulfate: 25% solution  
Sodium chloride : 5% solution  
Ammonium fluoride : 30% solution (stored in a plastic bottle)  
Nitric acid : specific weight 1.42

Manganese standard solution: take 1 gram of pure manganese and add 15 milliliters of 1:1 nitric acid. Heat in a low temperature electric furnace and boil to eliminate the nitrogen oxide. Cool and transfer into a 1,000 milliliter volumetric flask. Dilute with water until calibration and shake evenly. Each milliliter of this solution contains 1 milligram of manganese.

Sodium arsenite - sodium nitrite standard solution: 0.02N. Place 1 gram of arsenic trioxide into a 400 milliliter beaker and add a 25 milliliter solution of 16% sodium hydroxide. Heat and dissolve at a low temperature and dilute with water to 200 milliliters. Neutralize with 2:3 sulphuric acid until slight acidity (test with litmus paper) and exceed 2-3 milliliters. Then neutralize with 15% sodium carbonate until the solution appears neutral. Add 1 gram of sodium nitrate and after dissolving, filter, dilute with water to 2,000 milliliters and shake evenly.

Use the following method to determine the titration of sodium arsenite - sodium nitrite standard solution on manganese:

Separate and place a standard solution of manganese (its quantity should be the same as the manganese content of the measured sample) in a 500 milliliter Erlenmeyer flask. Add 10 milliliters of 1:1 sulphuric acid, drip in 1 drop of hydrofluoric acid, add 50 milliliters of water and 5 milliliters of 1% silver nitrate ..... carry out according to the analysis

procedure.

The titration of the sodium arsenite - sodium nitrite standard solution on manganese is calculated by the following formula:

$$T = \frac{g}{v}$$

In the formula: g is the weight (milligrams) of manganese contained in the manganese standard solution; v is the volume (milliliters) of sodium arsenite - sodium nitrite standard solution consumed during titration.

### 3. Analysis Procedure

Place a 0.25 - 0.50 gram sample (containing 0.1 - 0.5% manganese weighing 0.5 grams; containing 0.5 - 2% manganese weighing 0.25 grams) in a 500 milliliter Erlenmeyer flask. Add 10-12 milliliters of sulphuric acid, 5 drops of hydrofluoric acid and heat and dissolve at a low temperature. After the sample is dissolved, drip in 3-5 drops of nitric acid and oxidize until the solution's purple color completely disappears. Boil to eliminate the nitrogen's oxide. Cool and add 500 milliliters of water, 50 milliliters of a 1% silver nitrate solution, 15 milliliters of a 25% ammonium persulfate solution and 10 milliliters of 30% ammonium fluoride. Heat and boil so that the manganese oxidizes into a purplish red permanganate. Continue to boil until anhydrous bubbles are produced. This will cause the ammonium persulfate to completely dissolve. Take down the Erlenmeyer flask, put aside for a short time and cool with running water. Add 10 milliliters of 2:3 sulphuric acid and 5

milliliters of a 1% sodium chloride solution. Titrate with the sodium arsenite - sodium nitrite standard solution until the solution's purplish red color disappears.

#### 4. Calculations

The manganese content is calculated by the following formula:

$$\text{Mn\%} = \frac{T \cdot V \cdot 100}{G}$$

In the formula: V is the volume (milliliters) of sodium arsenite - sodium nitrite solution consumed during titration; T is the titration (milligrams/milliliter) of sodium arsenite - sodium nitrite on manganese; G is the sample's weight (milligrams).

#### 5. Allowable Deviation

Manganese Content %	Allowable Deviation %
0.1 - 1.0	$\pm 0.015$
1.0 - 2.0	$\pm 0.025$

#### Notes:

(1) We should avoid bringing in chlorine ions during the operation process prior to oxidation.

(2) We should avoid boiling for a long time after permanganate is produced so as to prevent the permanganate from dissolving.

(3) The percentage content of manganese cannot be calculated according to a theoretical value but during the operation process we must use pure manganese (its quantity should be close to that of the manganese in the sample) to calibrate the

sodium arsenite - sodium nitrite standard solution and use the titration degree to calculate the content of manganese.

(4) If the manganese content in the sample is less than 2%, we cannot add ammonium fluoride during oxidation.

## STANDARD FOR THE DETERMINATION OF CHROMIUM IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

### 1. Summary of Method

In a sulphuric acid medium, using silver nitrate as the indicator, add ammonium persulfate to oxidize the three valence chromium into six valence chromium. At the same time, manganese is oxidized into permanganate and added to decompose the mendelevium chloride. Then use phenyl substituted amino benzoic acid as the indicator and titrate with an ammonium ferrous sulfate standard solution until the solution assumes a green color. Calculate the content of chromium based on the amount of ammonium ferrous sulfate standard solution consumed.

Determination range: 1.00 - 12.00%.

### 2. Reagent

Sulphuric acid	: 1:1
Nitric acid	: specific weight 1.42
Silver nitrate	: 1% solution
Ammonium persulfate	: 25% solution (newly made)
Sodium chloride	: 5% solution
Manganese sulfate	: 5% solution

Phenyl substituted amino benzoic acid: 0.2% solution.

Dissolve 0.2 grams of phenyl substituted amino benzoic acid and 0.2 grams of sodium carbonate in 100 milliliters of hot water.

Chromium standard solution: take 2.8288 grams of standard



weight potassium chromate (first stove in  $140^{\circ}$ - $150^{\circ}$ C), dissolve by adding water and then transfer into a 1,000 milliliter volumetric flask. Dilute with water until calibration and shake evenly. Each milliliter of this solution contains 1 milligram of chromium.

Ammonium ferrous sulfate standard solution: 0.1N. Dissolve 39.22 grams of ammonium ferrous sulfate into water, dilute until calibration and shake evenly.

Titration of the ammonium ferrous sulfate standard solution on chromium: take 20 milliliters of chromium standard solution, add 50 milliliters of 5:95 sulphuric acid and 5 drops of a 0.2% phenyl substituted amino benzoic acid solution. Titrate with a 0.1N ammonium ferrous sulfate standard solution until the solution changes from purplish red to green.

The titration degree of the ammonium ferrous sulfate standard solution on chromium is expressed by T and calculated by the following formula:

$$T = \frac{g}{v}$$

In the formula: g is the weight (milligrams) of the chromium contained in the potassium dichromate standard solution: v is the volume of ammonium ferrous sulfate standard solution consumed during titration.

### 3. Analysis Procedure

Place a 0.2 gram sample in a 500 milliliter Erlenmeyer flask, add 20 milliliters of 1:1 sulphuric acid, heat and

dissolve. Drip in nitric acid and oxidize until the solution's purple color disappears. Boil and evaporate until the sulphuric acid emits smoke and after cooling add 150 milliliters of water. Heat and dissolve the salt and add 2 drops of a 5% manganese sulfate solution, 5 milliliters of a <sup>1%</sup> silver nitrate solution and 15 milliliters of a 25% ammonium persulfate solution. Heat and boil until the small air bubbles disappear so that manganese and chromium oxidation is completed. Take down and add 5-10 milliliters of a 5% sodium chloride solution and continue to boil for 3 minutes until the purplish red color disappears. Cool to room temperature. Add 5 drops of a 0.2% phenyl substituted amino benzoic acid solution and titrate with a 0.1N ammonium ferrous sulfate standard solution until the solution changes from purplish red to green.

#### 4. Calculations

The percentage content of chromium is calculated by the following formula:

$$\text{Cr\%} = \frac{T \cdot V}{G} \times 100$$

In the formula: T is the titration degree (milligrams/milliliter) of ammonium ferrous sulfate standard solution on chromium; V is the volume (milliliters) of ammonium ferrous sulfate standard solution consumed; G is the sample's weight (milligrams).

#### 5. Allowable Deviation

Chromium Content %	Allowable Deviation %
1.0 - 3.0	$\pm 0.05$
3.0 - 7.0	$\pm 0.10$
7.0 - 12.0	$\pm 0.15$

Notes:

(1) When there is vanadium in the sample, we should subtract the equivalent amount of vanadium in the chromium from the calculation results. 1% vanadium is equivalent to 0.34% chromium.

(2) After the sulphuric acid emits smoke, before adding the silver nitrate and oxidizing the ammonium persulfate, it is necessary to prevent chlorine ions from entering into the solution so as to avoid the effect of completely oxidizing the chromium and manganese.

(3) We need not add manganese sulfate when the sample contains manganese.

(4) Because the indicator, a phenyl substituted amino benzoic acid solution, has reductibility, it is better to use a small quantity and the quantity used during calibration and analysis operations should be the same.

## II. The Diphenylamine Carbamide Absorption Luminosity Method

### 1. Main Points of Method

In a sulphuric acid medium, use a cupferron reagent to separate copper ferrimanganese and molybdenum which is equivalent to disturbing the elements. Decompose the organic phase with nitric acid and perchlorate. When there is silver nitrate, the ammonium persulfate oxidizes the chromium to six valence

and in a 0.2N sulphuric acid solution, the six valence chromium and diphenylamine carbamide form a stable colored complex. The chromium content is determined by the darkness of the color.

Determination range: 0.10 - 2.00%.

## 2. Reagent

Sulphuric acid	: 1:1; 1:20
Nitric acid	: specific weight 1.42
Perchlorate	: 70%
Anhydrous alcohol	: analytically pure
Cupferron reagent	: 5% solution
Silver nitrate	: 2% solution
Ammonium persulfate	: 2% solution
Urea	: 10% solution
Sodium nitrite	: 4% solution

Diphenylamine carbamide: 0.5% alcohol solution. Dissolve 2 grams of phthalic anhydride in 100 milliliters of anhydrous alcohol, heat and dissolve. Accurately add in 0.5 grams of diphenylamine carbamide and shake until dissolved. Transfer into a brown reagent bottle and store for future use.

Chromium standard solution: prepare 1.136 grams of potassium dichromate in a 150°C stove and dissolve in a small amount of water. Transfer into a 1,000 milliliter volumetric flask, dilute with water until calibration and shake evenly.

Dissolve 50 milliliters of the solution into a 1,000 milliliter volumetric flask, dilute with water until calibration and shake evenly. Each milliliter of this solution contains 0.2 milligrams of chromium.

## 3. Analysis Procedure

Put a 0.1 gram sample in a 100 milliliter beaker, add 10 milliliters of 1:1 sulphuric acid, heat and dissolve. Drip in

nitric acid and oxidize until the solution's purple color disappears. Continue to evaporate until the sulphuric acid emits smoke and cool. Rinse the beaker with a small amount of water, transfer into a 100 milliliter volumetric flask and dilute with water to 50 milliliters. Add 30 milliliters of a 5% cupferron reagent solution, dilute with water until calibration and shake evenly. Put aside for 10-15 minutes and then filter in a dry Erlenmeyer flask.

Separate 20 milliliters of filtered solution in a 150 milliliter Erlenmeyer flask. Add 3 milliliters of nitric acid and 3 milliliters of perchlorate, heat until thick white smoke is emitted for 3 minutes and then cool. Rinse the beaker walls with a small amount of water, dilute with water to about 30 milliliters and heat to near boiling. Add 10 drops of a 2% silver nitrate solution and 5 milliliters of a 2% ammonium persulfate solution. Boil until air bubbles are produced and then cool. Transfer into a 200 milliliter volumetric flask, dilute to about 180 milliliters and add 5 milliliters of a 0.5% diphenylamine carbamide. Dilute with water until calibration and shake evenly. Put aside for 5 minutes and then use a 1-3 centimeter colorimetric plate to measure the absorption luminosity in a 550 millimicrometer wavelength area. Find the chromium content from the standard curve.

#### 4. Calculations

The percentage content of chromium is calculated by the following formula:

$$\text{Cr\%} = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight of the chromium found on the standard curve;  $G$  is the weight of the sample contained in the developing solution.

#### 5. Drawing of the Standard Curve

Separately add 0, 0.5, 2.0, 4.0, 6.0, 8.0 and 10.0 milliliters of chromium standard solution into several 200 milliliter volumetric flasks. Add 20 milliliters of 1:20 sulphuric acid, add water to 180 milliliters and accurately add 5 milliliters of a 0.5% diphenylamine carbamide solution. Dilute with water until calibration and shake evenly. Put aside for 5 minutes and then carry out according to the analysis procedure. Measure the absorption luminosity and draw the standard curve.

#### 6. Allowable Deviation

Chromium Content %	Allowable Deviation %
0.1 - 0.5	$\pm 0.02$
0.5 - 1.0	$\pm 0.05$
1.0 - 2.0	$\pm 0.07$

#### Notes:

(1) When adding a cupferron reagent, the temperature should be controlled to below  $15^{\circ}\text{C}$ .

(2) When the perchlorate decomposes the organic reagent, the temperature should not be too high.

(3) When there is a 1-2% chromium content, separate 10 milliliters of filtered solution into a 200 milliliter volumetric flask and then add 10 milliliters of sulphuric acid (1:20).

(4) The volume after oxidation should not be less than 25 milliliters.

(5) If there is manganese, add 5 milliliters of a 10% urea solution, drip in a 4 % sodium nitrite solution and reduce to colorless.

STANDARD FOR THE DETERMINATION  
OF COPPER IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

I. The Copper Reagent Absorption Luminosity Method

1. Summary of the Method

In a sulphuric acid medium, use citric acid to complex titanium iron and aluminum and then titrate to an ammonia. Use animal glue as the stabilizer and then the copper and copper reagent produce a brownish yellow suspension. The copper content is determined according to the darkness of the color.

Determination range: 1.0 - 5.0%.

2. Reagents

Sulphuric acid: 1:1  
Nitric acid : specific weight 1.42: 1:1  
Citric acid : 10% solution  
Animal glue : 0.5% solution  
Copper reagent: 0.5% solution  
Ammonia water : specific weight 0.9

Copper standard solution: place 0.1 grams of pure copper in a 200 milliliter beaker, add 10 milliliters of 1:1 nitric acid, heat and dissolve. Then add 10 milliliters of 1:1 sulphuric acid, heat and evaporate until the sulphuric acid emits smoke, then cool. Add 50 milliliters of water and heat and dissolve the salt. Transfer to a 1,000 milliliter volumetric flask, dilute with water until calibration and shake evenly. Each milliliter of this solution contains 0.1 milligrams of copper.



### 3. Analysis Procedure

Place a 1 gram sample in a 200 milliliter beaker, add 10 milliliters of 1:1 sulphuric acid and heat so that the sample completely dissolves. Then drip in nitric acid to oxidize the three valence titanium until the purple color disappears. Continue to heat until the sulphuric acid emits smoke, then cool. Add in 50 milliliters of water, boil so that the salt is completely dissolved and cool. Transfer into a 100 milliliter volumetric flask, dilute with water to calibration and shake evenly.

Separate 10 milliliters of the above solution into a 100 milliliter volumetric flask. Add 10 milliliters of a 10% citric acid solution, 10 milliliters of a 0.5% animal glue solution and 10 milliliters of ammonia water. Add in 5 milliliters of a 0.5% copper reagent solution with continual shaking, dilute with water to calibration and shake evenly. Use a 1 centimeter colorimetric dish to measure the absorption luminosity in a 440 millimicrometer wavelength area and find the copper content from the standard curve.

Reference solution: the same as the reference solution of the standard curve.

### 4. Calculations

The percentage content of copper is calculated by the following formula:

$$\text{Cu} = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the copper

found on the standard curve; G is the weight (milligrams) of the sample contained in the color solution.

#### 5. Drawing of the Standard Curve

Separately add 0, 1.0, 2.0, 3.0, 4.0 and 5.0 milliliters of copper standard solution into several 100 milliliter volumetric flasks as well as 10 milliliters of a 0.5% animal glue solution. Carry out according to the analysis procedure taking the reagent blank as the reference solution. Measure the absorption luminosity and draw the standard curve.

#### 6. Allowable Deviation

Copper Content %	Allowable Deviation %
1.0 - 2.0	$\pm 0.05$
2.0 - 5.0	$\pm 0.10$

#### Note:

When there is a 4% chromium content a disturbance occurs so that the test solution itself becomes a blank. Separate 10 milliliters of the sample solution into a 100 milliliter volumetric flask, add 10 milliliters of a 10% citric acid solution, 10 milliliters of a 0.5% animal glue solution and 10 milliliters of ammonia water. Dilute with water until calibration and shake evenly. Use this as the reference solution and to eliminate disturbance.

## II. The Double Ring Hexanone Oxamide Dihydrazone Absorption Luminosity Method

### 1. Summary of Method

Double ring hexanone oxamide dihydrazone and copper produce a blue colored complex in an ammonia solution with a

pH of 8.7 - 9.5. The copper content is measured by the darkness of the color.

Determination range: 0.10 - 1.00%.

## 2. Reagent

Sulphuric acid	: 1:1
Nitric acid	: specific weight 1.42
Ammonium citrate	: 50% solution
Phenol red indicator:	0.05% alcohol solution
Ammonia water	: specific weight 0.9
Buffer solution	: pH-9.3

Add 54 grams of ammonium chloride into 63 milliliters of ammonia water. Dilute with water to a 1,000 milliliter volumetric flask and shake evenly.

Double ring hexanone oxamide dihydrazone solution: 0.01%.  
Add 1 gram of double ring hexanone oxamide dihydrazone abbreviated as BCO) into 100 milliliters of alcohol and 100 milliliters of hot water. After shaking and dissolving dilute with water to 1,000 milliliters and shake evenly.

Copper standard solution: add 0.1 grams of pure copper into 10 milliliters of 1:1 nitric acid, heat and dissolve, then cool. Transfer into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly.

Separate 50 milliliters of the above solution into a 100 milliliter volumetric flask, dilute with water to calibration and shake evenly. Each milliliter of this solution contains 0.05 milligrams of copper.

## 3. Analysis Procedure

Place a 0.5 gram sample in a 150 milliliter beaker, add 15 milliliters of 1:1 sulphuric acid, heat and dissolve. Drip in

nitric acid and oxidize until the solution's purple color disappears. Boil to eliminate the oxide of the nitrogen and cool. Transfer into a 100 milliliter beaker, dilute with water to calibration and shake evenly.

Separate 5 milliliters of the above solution into a 100 milliliter volumetric flask, add 5 milliliters of a 50% ammonium citrate solution and 2 drops of 0.05% phenol red indicator. Neutralize with ammonia water until it assumes a red color and add an extra 4 drops. Then add 5 milliliters of buffer solution, cool to room temperature and add 15 milliliters of 0.1% BCO solution. Dilute with water to calibration and shake evenly. Put aside for 5 minutes, measure the absorption luminosity in a 560 millimicrometer wavelength area with a 1 centimeter colorimetric dish and find the copper content from the standard curve.

Reference solution: the same as the reference solution of the standard curve.

#### 4. Calculations

The percentage content of copper is calculated by the following formula:

$$\text{Cu} = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the copper found on the standard curve;  $G$  is the weight (milligrams) of the sample contained in the color solution.

#### 5. Drawing of the Standard Curve

Separately add 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 milliliters of copper standard solution into several 100

milliliter volumetric flasks. Add 5 milliliters of a 50% ammonium citrate solution and 2 drops of 0.05% phenol red indicator ..... carry out the following according to the analysis procedure. Measure the absorption luminosity and draw the standard curve.

#### 6. Allowable Deviation

Copper Content %	Allowable Deviation %
0.10 - 0.25	$\pm 0.015$
0.25 - 0.50	$\pm 0.025$
0.50 - 1.00	$\pm 0.05$

#### Notes:

(1) When the sample contains chromium, the sample itself is used as the blank. Separate 5 milliliters of the sample solution into a 100 milliliters volumetric flask and add 5 milliliters of a 50% citric acid solution .... carry out the following according to the analysis procedure. Do not add a BCO chromophoric agent. Use this as the reference solution to eliminate interference.

(2) When the sample's vanadium content exceeds 6%, add 20 milliliters of BCO and take the sample solution itself as the blank (same as note (1)) in order for the reference solution to eliminate interference.

STANDARD FOR THE DETERMINATION  
OF BORON IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Material)

I. The Methylene Blue - 1.2 Dichloroethane Extraction  
Absorption Luminosity Method

1. Summary of Method

In a sulphuric acid medium, boron and hydrofluoric acid produce borofluorine ions and the methylene blue reaction produces a methylene blue borofluorine compound. This compound can be extracted by 1.2 - dichloroethane and the boron content is measured according to the darkness of color.

Determination range: 0.005 - 0.030%.

2. Reagents

Sulphuric acid (very pure): 1:1  
Hydrofluoric acid (first degree): 5%

Add 100 milliliters of 40% hydrofluoric acid in a plastic bottle with 700 milliliters of water and then shake evenly.

Methylene blue: 0.001M. Dissolve 0.374 grams of methylene blue in water, filter in a 1,000 milliliter volumetric flask, dilute with water to calibration and then shake evenly.

Potassium permanganate: 0.1M. Dissolve 15.8 grams of potassium permanganate in a small amount of water, transfer into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly.

Hydrogen peroxide: 30%

Ammonium ferrous sulfate : 4% solution. Dissolve 4 grams of ammonium ferrous sulfate in water. Drip in 4 drops of 1:1 sulphuric acid and dilute with water to 100 milliliters.

1.2 - dichloroethane (first degree).

Boron standard solution: dissolve 0.0572 grams of boric acid (spectrum pure) in water. Transfer into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly. Each milliliter of this solution contains 0.01 milligrams of boron.

Draw 50 milliliters of the above solution into a 500 milliliter volumetric flask, dilute with water to calibration and shake evenly. Each milliliter of this solution contains 0.001 milligrams of boron.

### 3. Analysis Procedure

Place a 0.1 - 0.5 gram sample in a 150 milliliter quartz beaker. Add 14 milliliters of 1:1 sulphuric acid and after heating and dissolving, drip in hydrogen peroxide and oxidize until the solution's purple color completely disappears. Clean the beaker wall with water and continue to boil until the hydrogen peroxide is completely dissolved, then cool. Transfer into a 100 milliliter volumetric flask, dilute with water to calibration and shake evenly.

Separate 10 milliliters of the solution into a 125 milliliter plastic bottle. Accurately add in 10 milliliters of water and 5 milliliters of 5% hydrofluoric acid and then shake evenly.

Add precisely 23 milliliters of water and 1-2 drops of a 0.1M potassium permanganate solution so that the solution assumes a slight red color. Then add in 2 milliliters of a 4% ammonium ferrous sulfate solution and reduce until the solution's red color disappears. Add 10 milliliters of 0.001M methylene blue and shake evenly. Add in precisely 25 milliliters of 1.2 - dichloroethane, shake for 2 minutes and after placing aside the separate layers eliminate the water phase. Draw 5 milliliters of the colored organic phase into a dry 25 milliliter volumetric flask. Add precisely 10 milliliters of 1.2 - dichloroethane and shake evenly.

Taking water as the reference solution, a 1 centimeter colorimetric dish is used to measure the absorption luminosity in a 660 millimicrometer wavelength area and subtract the absorption luminosity of the reagent blank. Find the boron content from the standard curve.

#### 4. Calculations

The percentage content of boron is calculated by the following formula:

$$B\% = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the boron found on the standard curve;  $G$  is the weight (milligrams) of the sample contained in the color solution.

#### 5. Drawing of the Standard Curve

Place 0.1 - 0.5 grams of a titanium alloy without boron in a 150 milliliter quartz beaker. Add in 14 milliliters of 1:1



sulphuric acid and after heating and dissolving, drip in 30% hydrogen peroxide until the solution's purple color completely disappears. Clean the beaker wall with water, continue to boil until the hydrogen peroxide is completely dissolved and then cool. Transfer into a 100 milliliter volumetric flask, dilute with water to calibration and shake evenly.

Draw 10 milliliters of the above solution and separately add 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 milliliters of boron standard solution into several 125 milliliter plastic bottles. Add in precisely 10 milliliters of water and 5 milliliters of hydrofluoric acid and then shake evenly. Set aside for one hour and then carry out according to the analysis procedure. Measure the absorption luminosity subtracting the absorption luminosity of the reagent blank and draw the standard curve.

#### 6. Allowable Deviation

Boron Content %	Allowable Deviation %
0.005 - 0.01	$\pm 0.0010$
0.01 - 0.03	$\pm 0.0025$

#### Notes:

(1) The instruments used must be one hundred percent clean and the operation must be meticulous.

(2) The reagent solutions used must be added accurately.

(3) Avoid contact with the nitric acid during the testing process.

(4) Samples containing niobium and tantalum should use the methyl alcohol distillation - curcumin absorption luminosity

method for determination.

## II. The Methyl Alcohol Distillation - Curcumin Absorption Luminosity Method

### 1. Summary of Method

In a phosphorus sulfate medium, boron and methyl alcohol produce methyl borate with a low boiling point. After being evaporated it combines with sodium hydroxide to produce sodium borate. Then, in a sulphuric acid - glacial acetic acid medium, boron and curcumin produce a red colored compound and we measure the boron content according to the darkness of the color.

Determination range: 0.001 - 0.050%.

### 2. Reagent

Sulphuric acid : highly pure reagent

Phosphoric acid: special purity

Sulphuric acid - glacial acetic acid: 1:1 mixed solution

Mixture of sulphuric and phosphoric acids: even mixture of 30 milliliters of 1:1 sulphuric acid and 70 milliliters of 1:1 phosphoric acid.

Curcumin : a 0.1% glacial acetic acid solution. Dissolve 0.1 grams of curcumin into 100 milliliters of glacial acetic acid and place in a plastic bottle.

Sodium hydroxide: 1N solution. Put 20 grams of sodium hydroxide into a plastic bottle and add 500 milliliters of water. After dissolving, shake evenly.

Methyl alcohol  
Acetone

Boron standard solution:

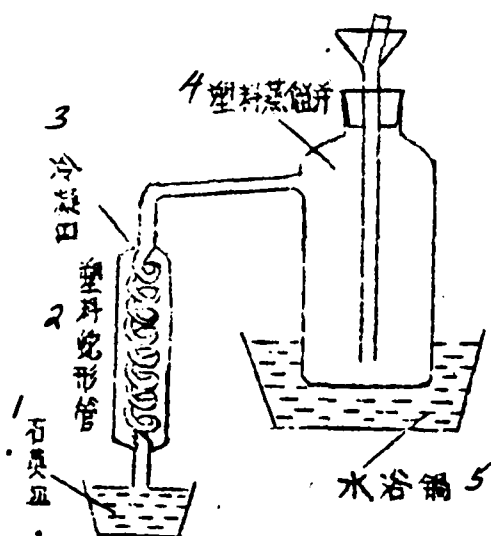
A Dissolve 0.5719 grams of boric acid (spectrum pure) in

water. Transfer into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly.

B Draw 20 milliliters of solution A into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly. Each milliliter of this solution contains 0.002 milligrams of boron.

C Draw 10 milliliters of solution A into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly. Each milliliter of this solution contains 0.001 milligrams of boron.

Polyethylene distillation apparatus (see figure below) water bath cauldron.



- Key: 1. Quartz dish  
2. Plastic S-shaped tube  
3. Cooling (? illegible)  
4. Plastic distillation bottle  
5. Water bath cauldron

### 3. Analysis Procedure

Put a 0.05 gram sample in a 100 milliliter quartz beaker and add 10 milliliters of mixed sulphuric and phosphoric acids. After heating at a low temperature and dissolving, continue to heat until the sulphuric acid emits a little smoke, then take down and cool and add 2 milliliters of water. After cooling, transfer into a distillation bottle. The beaker and surface dish are rinsed four times in the distillation bottle with 20 milliliters of methyl alcohol. Afterwards, the bottle plug is put in tightly (it cannot leak gas) and the solution in the bottle is shaken evenly. The exit of the distillation bottle is connected to the cooling tube and the lower end of the cooling tube is immersed in the quartz dish with an (acid absorbing solution: 2.5 milliliters of 1N sodium hydroxide solution with 7.5 milliliters of water added). The distillation bottle is placed in the water bath. Open up the cooling tube, then open up the water bath electric furnace and carry out distillation. After all of the methyl alcohol evaporates (the exhaust tube of the distillation bottle becomes dry), close the electric furnace and open the small stopper on the upper end of the distillation bottle. Then add 15 milliliters of methyl alcohol and shake evenly. Open the water bath electric furnace to carry out distillation and after the methyl alcohol completely evaporates add 10 milliliters of methyl alcohol in order to carry out distillation again. Clean

the cooling tube with a small amount of water. Place the quartz dish with an absorbing solution on a constant temperature bath. Its temperature should not be higher than 90°C. The solution is evaporated until it descends to the quartz dish. Add in 3 milliliters of a 0.1% curcumin solution and after the salt completely dissolves add 3 milliliters of sulphuric acid - glacial acetic acid. Place in a constant temperature water bath. A temperature of 45°C is maintained for 20 minutes. After taken down to cool, 1:1 ketone is used for washing in a 100 milliliter volumetric flask. Dilute to calibration and shake evenly. Water is used as the reference solution and the absorption luminosity is measured with a 1 centimeter colorimetric dish in a 550 millimicrometer wavelength area. Then find the boron content on the standard curve.

#### 4. Calculations

The percentage content of boron is calculated by the following formula:

$$B\% = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the boron found on the standard curve;  $G$  is the weight (milligrams) of the sample contained in the color solution.

#### 5. Drawing of the Standard Curve

Separately place 0, 1.0, 2.0, 3.0, 4.0 and 5.0 milliliters of boron standard solution C in 100 milliliter quartz beakers. Add in 10 milliliters of sulphuric and phosphoric mixed acid, heat and evaporate until the sulphuric acid emits smoke. After

taking down and cooling, add 2 milliliters of water and transfer into the distillation bottle. Carry out the following according to the analysis procedure and draw the standard curve.

#### 6. Allowable Deviation

Boron Content %	Allowable Deviation %
0.001 - 0.005	$\pm 0.0005$
0.005 - 0.010	$\pm 0.001$
0.010 - 0.050	$\pm 0.003$

#### Notes:

(1) When the acid absorbing solution with methyl alcohol evaporates, the temperature of the water bath should not exceed 90°C otherwise there can be a loss of boron and thus lower results.

(2) After adding in curcumin, the salt should be dissolved completely. Further, add sulphuric acid - glacial acetic acid otherwise it can affect results.

(3) When adding curcumin color, it should not come in contact with the acid-base steam so as to avoid it affecting the results.

(4) The distillation device which stringently prevents leaking gas should be examined beforehand.

(5) If there is no good phosphoric acid, we can carry out cleansing. The cleansing method is as follows:

Place 30 milliliters of phosphoric acid in a 200 milliliter quartz beaker. Draw a calibrated line on the beaker wall aimed at the solution surface of the phosphoric acid in the beaker. Add 50 milliliters of methyl alcohol and stir evenly with a plastic rod. (It is best that the quantity of methyl alcohol be 0.5 times greater than the quantity of phosphoric acid). Heat

and evaporate at a low temperature until the methyl alcohol is eliminated, take down and cool. Then add 30 milliliters of methyl alcohol mixed evenly, evaporate until the methyl alcohol is eliminated and after repeating distillation twice, take down and cool. Dilute with blowing water to the graduated line of the phosphoric acid's original volume, then shake evenly.

STANDARD FOR THE DETERMINATION  
OF CERIUM IN TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

THE PMBP Extraction - Azoarsenic  
III Absorption Luminosity Method

1. Summary of Method

In a 10% sulphuric acid solution, use a cupferron reagent and trichloromethane extraction to separate the titanium, tin, zirconium and niobium. In a solution with pH=5.1-5.5, use PMBP to extract cerium and then use an azoarsenic III solution for back extraction. The azoarsenic III and cerium produce a purplish red complex. The cerium content is determined according to the darkness of the color.

Determination range: 0.01 - 0.20%.

2. Reagent

Sulphuric acid: 1:1

Nitric acid : specific weight 1.42

PMBP (1-phenyl-3-methyl-4-phenacyl pyrazolon): 0.1M benzene solution. Dissolve 3 grams of PMBP in 100 milliliters of benzene, transfer into a 500 milliliter separatory funnel and use 100 milliliters of 1:5 hydrochloric acid and shake for several minutes to eliminate the water phase. Then wash 3-4 times with water to eliminate the small amount of calcium in the PMBP. Finally,



eliminate the water phase and dilute with benzene to 1,000 milliliters.

Azoarsenic III: 0.1% solution.

Sulfosalicylic acid: 10% solution (regulate the acidimeter with a 20% sodium hydroxide solution to pH-2.4).

Chloroethanoic acid: 10% solution (regulate the acidimeter with a 20% sodium hydroxide solution to pH-2.4).

Azoarsenic III back extraction solution: add 50 milliliters of a 0.1% azoarsenic III solution; 100 milliliters of a sulfosalicylic acid solution and 100 milliliters of a 10% chloroethanoic acid solution into a 1,000 milliliter volumetric flask. Dilute with water to calibration and shake evenly. Finally, this solution has a pH equal to 2.5.

Acetic acid - sodium acetate buffer solution: dissolve 136 grams of crystalline sodium acetate in water and dilute with water to 500 milliliters. Regulate the acidimeter with glacial acetic acid until the pH reaches 5.5 (requires about 8 milliliters of glacial acetic acid).

Dimethyl xanthine: 0.1% alcohol solution.

Cupferron reagent: 10% solution (newly composed).

Trichloromethane  
Ascorbic acid: solid

Cerium standard solution: put 0.1228 grams of spectrum pure cerium oxide in a 200 milliliter beaker. Add 20 milliliters of 1:1 sulphuric acid and evaporate until the sulphuric acid emits smoke so as to oxidize the cerium and transform it into cerium sulfate. Dissolve with water and transfer into a 1,000 milliliter

volumetric flask. Dilute with water to calibration and shake evenly. Separate 20 milliliters of the above solution into a 1,000 milliliter volumetric flask, dilute with water to calibration and shake evenly. Each milliliter of this solution contains 0.002 milligrams of cerium.

### 3. Analysis Procedure

Place a 0.1 gram sample in a 100 milliliter beaker, add 20 milliliters of 1:1 sulphuric acid and heat until the sample is completely dissolved. Oxidize with nitric acid until the solution's purple color disappears. Evaporate until the sulphuric acid emits smoke, then cool. Add a small amount of water for dissolving, transfer to a 100 milliliter volumetric flask, dilute with water to calibration and shake evenly.

Draw 10 milliliters of the above solution into a 125 milliliter separatory funnel, add 2 milliliters of a 10% cupferron reagent solution and 15 milliliters of trichloromethane and shake for one minute. After setting aside the separate layers, eliminate the organic phase, then rinse with trichloromethane once. Drip in 2 drops of a 0.1% dimethyl xanthine solution, neutralize with 1:1 ammonia water until close to a yellow color and then neutralize with 1:9 ammonia water until a yellow color appears. Afterwards, neutralize with 1:1 sodium chloride until a red color appears and then add an additional one drop. Add 2 milliliters of a 10% sulfosalicylic solution, 5 milliliters of a acetic acid - sodium acetate buffer solution and 15 milliliters of PMBP benzene solution and shake for

one minute. After laying aside the separate layers, eliminate the water phase. Rinse the organic phase with water once or twice, add a small amount of ascorbic acid, add precisely 10 milliliters of an azoarsenic III back extraction solution and shake for one minute. After placing aside the separate layers, use a small amount of absorbent cotton to stop up the lower opening of the separatory funnel and then filter the water phase in a dry 25 milliliter beaker. Water is taken as the reference solution. Use a 1 centimeter colorimetric dish to measure the absorption luminosity in a 660 millimicrometer wavelength area, subtract the blank value and then find the cerium content from the standard curve.

#### 4. Calculations

The percentage content of cerium is calculated by the following formula:

$$\text{Ce\%} = \frac{G_1}{G} \times 100$$

In the formula:  $G_1$  is the weight (milligrams) of the cerium found on the standard curve;  $G$  is the weight (milligrams) of the sample contained in the color solution.

#### 5. Drawing of the Standard Curve

Separate and add 0, 1, 2.5, 7.5 and 10 milliliters of cerium standard solution into six 125 milliliter separatory funnels and dilute with water until about 10 milliliters. Drip in 2 drops of dimethyl xanthine and carry out the following according to the analysis procedure. Measure the absorption luminosity and draw the standard curve after subtracting the reagent blank.

## 6. Allowable Deviation

Cerium Content %	Allowable Deviation %
0.010 - 0.025	$\pm 0.0025$
0.025 - 0.05	$\pm 0.005$
0.050 - 0.10	$\pm 0.010$
0.10 - 0.20	$\pm 0.015$

### Notes:

(1) After separation of the cupferron reagent extraction, the water phase should be colorless proving the separation is complete.

(2) After PMBP extraction, the water phase should have a pH of 5.1 - 6.0.

(3) When mixing the acidity, it is necessary to continuously drip in 1:1 ammonia water to prevent local overconcentration. The formation of sediment will produce lower deviations.

(4) When the cerium content in the sample is less than 0.01%, place 0.5 grams of the sample in a 200 milliliter beaker, add in 45 milliliters of 1:1 sulphuric acid and heat until dissolved. After dissolving, drip in nitric acid and oxidize until the solution's purple color completely disappears and the sulphuric acid emits smoke and then cool. Transfer into a 100 milliliter volumetric flask, dilute with water to calibration and shake evenly.

Draw 10 milliliters of the above solution into a 125 milliliter separating funnel, add 10 milliliters of a 10% cupferron reagent solution and 15 milliliters of trichloromethane and shake for 2 minutes. After separating the layers, eliminate the organic phase, then add in 10 milliliters of trichloromethane

and rinse once or twice. Drip in 2 drops of a 0.1% dimethyl xanthine solution and neutralize with 1:1 ammonia water until near a yellow color. Then neutralize with 1:9 ammonia water until a yellow color appears. Afterwards, neutralize with 1:1 hydrochloric acid until a red color appears and then add an additional 1 drop. Add 2 milliliters of 10% ascorbic acid and 5 milliliters of a acetic acid - sodium acetate buffer solution.

STANDARD FOR THE DETERMINATION OF NITROGEN  
IN TITANIUM AND TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

The Steam Distillation Method

1. Summary of Method

The sample is dissolved by hydrochloric acid and hydrofluoric acid. The combined nitrogen produces ammonium salt and for the volumetric method, under the action of a very strong alkali, the distilled ammonium salt separates out the nitrogen which is absorbed by the boric acid solution. Afterwards, a methyl red - methylene blue solution is used as the indicator and a hydrochloric acid (or sulphuric acid) standard solution is used for titration. De-ionized water absorption was used for the light absorbance method and determination was carried out after the added naphthalene reagent shows color.

Determination range: 0.001-0.5%

2. Reagent

Hydrochloric acid: specific weight 1.19,1:1;  
Hydrofluoric acid: 40%;  
Perchloric acid: 70%;  
Sulphuric acid: 1.4;  
Boric acid: very pure, saturated solution  
(or 0.1%)

Sodium hydroxide solution: 50%.

Dissolve 500 grams of sodium hydroxide into 1,100 milliliters of water, add about 0.5 grams of copper - aluminum alloy, mix, heat and boil until the solution is clear. Maintain a volume of 1,000 milliliters and after cooling store in a plastic contained for reserve.

Methyl red - methylene blue mixed indicator: dissolve 0.125 grams of methyl red and 0.083 grams of methylene blue in 100 milliliters of dehydrated alcohol. After being dissolved, store in a brown dripping flask and it can be used after 3 days.

(3 lines illegible ?).

Demarcation: place the sodium carbonate in a high temperature furnace at  $270-300^{\circ}\text{C}$  and heat for 2-2.5 hours. Place in a desiccator and cool to room temperature. Before the heated sodium carbonate is prepared a second time, we should heat it again for 2-3 hours in an oven at  $140-150^{\circ}\text{C}$ . 0.1400-0.1500 grams of prepared sodium carbonate (demarcated about 0.1N hydrochloric acid standard solution) are carefully placed in a slightly oblique Erlenmeyer flask. About 50 milliliters of water is added and shaking causes it to completely dissolve. A drop of 0.1% methyl orange is added and 0.1N hydrochloric acid is used for titration. With constant shaking it drops into a solution and suddenly changes from a yellow to orange color, that is, the slight red color in the yellow (the depth of the red color should be the same as the acid standard color) is the final point. At the same time, it is necessary to carry out blank tests.

Calculation:

$$N = \frac{G}{fv} = \frac{G}{0.052994V}$$

Sodium carbonate standard reagent, gram equivalent =  $\frac{M}{2} = 52.994$ .

In the formula: G - the weight (grams) of the sodium carbonate;

f - milligram equivalent value of the sodium carbonate (0.052994);

V - volume of consumed acid solution (milliliters).

Nitrogen standard solution: 0.3820 grams of ammonium chloride are baked for one hour at 110°C, dissolved in water, put into a 1,000 milliliter volumetric flask and it is diluted by water until calibration and shaken evenly. One milliliter of this solution contains 0.1 milligrams of nitrogen.

Napthalene reagent: dissolve 17 grams of mercury dichloride in 300 milliliters of water and dissolve 35 grams of potassium iodide in 100 milliliters of water. Afterwards, slowly pour the mercury dichloride solution into the potassium iodide solution (until a small amount of unsoluble red sediment appears). Then add in 600 milliliters of 20% potassium hydroxide solution, stir evenly and store in a brown flask in a dark place. After three days the top layer is used.

### 3. Apparatus

In principle, the steam distillation apparatus as shown in figure 1 (Note 1). This apparatus is made of hard glass and has ten parts. Among these, there are five small outlet terminals of the steam input tube inserted in the distillation bottle.



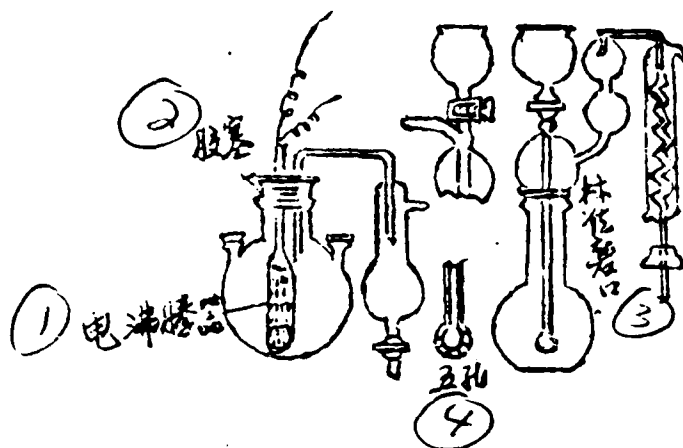


Fig. 1 Steam Distillation Nitrogen Fixing Apparatus (Made of Hard Glass)

- Key: 1. Electric boiling apparatus  
 2. Rubber plug  
 3. (? illegible)  
 4. Five holes

4. Analytic: Procedure  
 4.1 Volumetric Method (suitable for measuring more than 0.01% nitrogen)

A 0.5-1.0 gram sample is placed in a 200 milliliter Erlenmeyer flask (Note 2) and added<sup>!!!</sup> into a 30 milliliter hydrochloric acid solution and four to six drops of hydrofluoric acid (about 0.25 milliliters) (Note 3). It is heated and dissolved on a sand bath and with slight cooling its volume reaches about 40 milliliters after using water to wash the flask wall.

After the apparatus blank tests are normal (Note 4), a

50 milliliter 50% sodium hydroxide solution is added into the Wurtz flask (Note 5). 20 milliliters of saturated boric acid solution are added into a 250 milliliter Erlenmeyer flask and one drop of indicator is added as the absorbent (distilled at the lower end of the tube and should seep 2-5 millimeters into the solution). The test solution moves from the funnel into the Wurtz flask. A small amount of water is used to clean the Erlenmeyer flask and funnel, the valve is shut off and distillation is carried out. When the gathered solution reaches 120 milliliters (Note 6), we take down the absorption flask and use a small amount of water to rinse the lower end of the Wurtz flask. Two drops of indicator are added into the distillate solution and with continuous shaking we use 0.005N hydrochloric acid standard solution (Note 7) for titration until the solution changes from a green to red color. A reagent blank test is carried out along with the test (Note 8).

The nitrogen percentage content is calculated by the following formula

$$N\% = \frac{N_o \times 14.01 \times V - V_{\text{white}}}{G \times 1,000} \times 100$$

In the formula:  $V - V_{\text{white}}$  are separately the titration sample and consumed hydrochloric acid standard solution volume (milliliters) when blank.

$N_o$  is the equivalent concentration of the hydrochloric acid standard solution;

14.01 is the gram equivalent of the nitrogen;

G is the weight of the sample (grams);

4.2 Light Absorbance Method (suitable for measuring 0.001-0.02% quantities of nitrogen).

The dissolving sample is prepared for solution the same way as in the capacity method only it is in a 100 milliliter volumetric flask. 10 milliliters of de-ionized water (Note 9) is added in (or 10 milliliters of 0.01N sulphuric acid solution is used) as the absorbing solution and distillation is carried out. When the quantity of solution in the volumetric flask reaches 90 milliliters, the lowered volumetric flask causes the outlet end of the distillation tube to separate from the solution and continuously drip several drops of solution. A small amount of water is used to rinse the lower end of the distillation tube and the volumetric flask is taken down. 5 milliliters of naphthalene reagent are added by the titration tube (Note 10). Use a small amount of water until calibration and shake evenly. Five minutes after color appears (Note 11), a 3 centimeter colorimetric dish is used as a reference solution for the similar operating reagent blank of the test sample. The light absorbancy is measured in a 420 millimicrometer (or 430 millimicrometer) wavelength area and we find the content of nitrogen from the standard curve.

The percentage content of nitrogen is calculated by the following formula:

$$N\% = \frac{G_1}{G_2} \times 100$$

In the formula:  $G_1$  is the nitrogen quantity found from the standard curve (milligrams);  $G_2$  is the weight of the sample (milligrams) contained in the solution with color.

#### 4.3 Drawing the Standard Curve

Separately take standard solutions (0.01 milligrams/milliliter) of 0, 2, 4, 6, 8 and 10 milliliters of nitrogen and separately place them in prepared 100 milliliter volumetric flasks containing 10 milliliters of de-ionized water (or 10 milliliters of 0.01N sulphuric acid solution). Add 70 milliliters of water and 5 milliliters of naphthalene, dilute to calibration and shake evenly. Next, operate according to the analysis procedure in 4.2 and draw the standard curve (when drawing a standard curve for a sample with 0.01-0.02% nitrogen use a standard solution of 0.02 milligrams/milliliter and operate according to the above procedure).

#### 5. Allowable Deviation

合 氮 量 % (1)	允 许 差 % (2)
0.001~0.002	±0.0002
0.0021~0.005	±0.0005
0.0051~0.01	±0.001
0.011~0.02	±0.002
0.021~0.10	±0.005
0.11~0.20	±0.010
0.21~0.50	±0.020

Key: 1. Percentage of nitrogen  
2. Allowable difference %

Notes:

(1) The heater in the distillation apparatus coils resistance wire around a refractory rod with a spiral notch. It is placed in a sealed glass sleeve wherein the heating block is not easily damaged and the blank is reduced. After connecting an appropriate transformer to regulate the heating, we can prevent a violent reaction in the Wurtz flask. Furthermore, by making the nitrogen ball as a pear shaped ball we can avoid the error of measuring the alkali solution being carried into the absorption solution with the steam.

(2) We can also use a polyethylene beaker as the sample container, yet it is necessary to heat the decomposition sample on the water bath.

(3) When there is difficulty with the test sample, especially when it contains high silicon and high niobium, we can increase the hydrofluoric acid (add about 0.5-1.0 milliliters). The sample can also use a 1:4, 20 milliliter sulphuric acid solution in a plastic bottle to drip in hydrochloric acid for dissolving. It can also use a 1:4, 50 milliliter sulphuric acid solution and by adding 4 drops of hydrochloric acid in a glass triangular flask it can dissolve the sample. We can also drip in one milliliter of hydrogen peroxide to destroy the carbide for samples with high carbon contents. Use of hydrochloric acid and hydrofluoric acid is better than using sulphuric acid and hydrofluoric acid for dissolving the test sample. The blank value is also lower.

(4) Prior to distillation, we add one drop of mixed indicator to 20 milliliters of saturated boric acid solution to test the apparatus blank and the purplish red color is unable to change to green. Also, when the consumed hydrochloric acid standard solution (0.005N) from the titration is smaller than 0.20 milliliters, this indicates that the apparatus is normal. Otherwise, distillation is continued until it is normal. When the light absorbance method is used, if the distillation solution and naphthalene reagent do not show color this can then be considered normal. For a new apparatus we should carry out recovery rate tests using a standard nitrogen solution.

(5) The amount of sodium hydroxide used should cause an excess of 10% after acid neutralization of the solution sample.

Generally, a 50 milliliter 50% sodium hydroxide solution is used.

(6) When the amount of distillate ammonia is about 50 milliliters, the ammonia is basically distilled. To be cautious, we determine the total solution distilled to the receiver as 120 milliliters for the volumetric method; for the light absorbance method, we determine that the total solution distilled to the volumetric flask reaches 90 milliliters because the nitrogen quantity is relatively low. The distillation speed is determined by the apparatus and test conditions. This apparatus completes distillation in about 10-15 minutes.

(7) As for the standard solution employed for the volumetric method, we can also use a 0.005N sulphuric acid standard solution.

(8) Blank tests should be the same as the test sample analysis conditions. The consumed hydrochloric acid standard solution for the reagent blank must not be larger than 0.30 milliliters.

(9) All of the tests used distilled water without ammonia or de-ionized water. It should be noticed that the de-ionized water cannot have any resin otherwise after distillation the amino radical can decompose and separate out the ammonia, causing the blank to suddenly rise and the test to fail. Determination of the nitrogen must be carried out in an atmosphere without ammonia. Thus, to determine the nitrogen it is best to have a special room.

(10) The color agent is slowly added in by the titration

tube and when the injection speed is quickened the results will be higher. Because the alkalinity is overly concentrated, there is no way to have specific color when there is turbidity. When the amount of color agent inserted is 4-6 milliliters (alkalinity is in the range of 0.09-0.13N), light absorbance is invariant and thus this method uses a 5 milliliter color agent.

(11) Colored complex compounds are stable. In room temperature, five minutes to one hour after showing color the light absorbance does not change.



# STANDARD FOR THE DETERMINATION OF HYDROGEN IN TITANIUM AND TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

## Inert Gas Melting-Gas Chromatography

### 1. Summary of Method

A titanium or titanium alloy sample is heated and melted with a tin bath in a small graphite crucible and releases carbon monoxide, nitrogen and hydrogen. The mixed gas is carried by the nitrogen carrying gas past the chromatographic heat conducting pool. Because of the carbon monoxide and nitrogen gas, there is a small difference in the heat conducting coefficient and therefore after being measured by the heat conducting detector, the output's dispatch number only displays a hydrogen peak on the chromatograph. Based on the size of the hydrogen peak we measure the hydrogen content in the sample.

Determination range: 10-200 ppm (Note 1).

### 2. Reagent, Instruments

Acetone : analytically pure;  
Ether : analytically pure;  
Nitrogen gas : 99.9% purity;  
Tin : 99.9% purity;  
Chromatographically pure graphite electrode rod:  
     $\phi$  10 millimeters;  
Fine file : used for cleaning the surface of the  
    sample;  
Hacksaw or shears: used for cutting the sample;  
Blower : can blow hot air to dry the sample.

### 3. Apparatus

High frequency - chromatographic hydrogen measuring apparatus

Heat source: a one thousand watt high frequency furnace (Note 2) has an induction coil which uses cooling water. The heating furnace tube has an outer diameter of  $\varphi \leq 30$  millimeters, the wall thickness of its quartz tube is 1-1.5 millimeters and its volume is 40 centimeters<sup>3</sup>.

The measured section and gas path: the measured section is composed of an electromagnetic valve, carrier gas system and chromatograph. The gas path is shown in fig. 1.

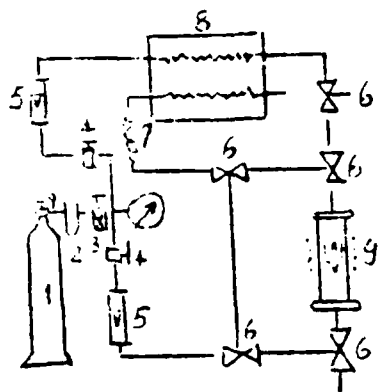


Fig. 1. Gas Path

- Key:
- 1. Nitrogen cylinder
  - 2. Purifier
  - 3. Stabilizing valve
  - 4. Circular valve
  - 5. Flowmeter
  - 6. Electromagnetic valve
  - 7. Chromatograph
  - 8. Heat conducting pool
  - 9. High frequency furnace
  - 10. Pressure meter

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STANDARD METHOD FOR ANALYZING GASES IN TITANIUM AND  
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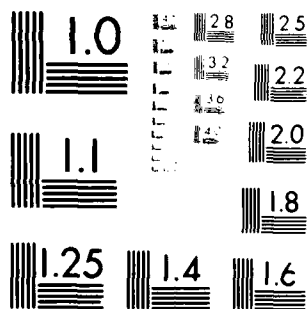
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MICROCOPY RESOLUTION TEST CHART  
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The control section: composed of four time delay relays, a switch and a contact relay. A chart of the circuit is shown in fig. 2.

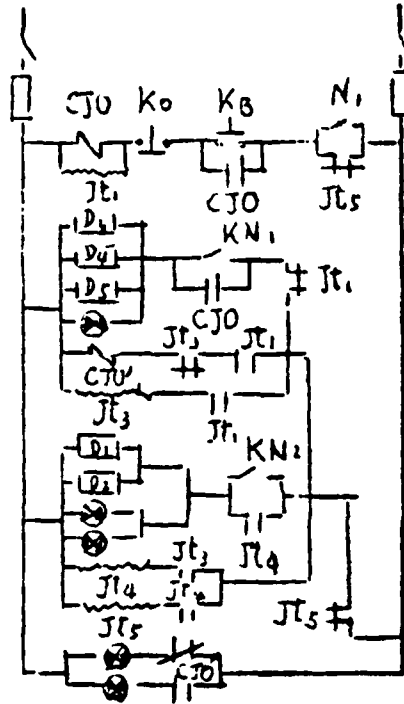


Fig. 2. Chart of the Circuit (? illegible)

#### 4. Analysis Procedure

##### 4.1 Making the Sampling and the Weight of the Sampling

An analytical sampling is made in a block form or board by slicing or cutting method. The processing of the manufactured analytical sampling produces a  $\phi 3 \times 3$  millimeter cylinder shape or another shape suitable for analysis. The surface of the sample is smooth. Prior to analysis, a fine file is

used to eliminate surface dirt and analysis is carried out after using acetone and ether, and cleaning and drying (a blowing can be used).

Preparations should be made for the sample's special materials based on analysis requirements. Aside from the cleaning process for the sample, a fault component sampling is not beneficial in carrying out other processes to avoid hydrogen content loss.

In principle, the weight of the sampling is made according to the following table.

Hydrogen Content (ppm)	Weight of Sample (G)
< 50	0.15 - 0.20
50 - 100	0.10 - 0.15
> 100	less than 0.10

#### 4.2 Analytical Conditions

Heating temperature: above 2,000°C;  
Heating time : 40 seconds;  
Bath material : tin;  
Bath ratio : over 1:5  
Chromatographic carrier gas flow speed:  
50-60 milliliters/minute;  
Carrier gas pressure: 10 Kg/Cm<sup>2</sup>;  
Chromatographic bridge flow: 100 milliamperes;  
Length of chromatographic column:  $\phi$  inner  
diameter 4 millimeters,  
length 0.5 meters;  
Molecular sieve : 5Å or 13x activation.

#### 4.3 Operation

Graphite crucible degassing: prior to analyzing the sample the graphite crucible (Note 3) must carry out degassing. The degassing temperature should be higher than the analytical temperature. This method must be higher than 2,000°C and the degassing time is 40 seconds.

Measuring the blank value: the graphite crucible equipped with flux is placed in the heating furnace tube and the carrier gas is used to rinse the furnace tube so as to eliminate the pollutants carried in air. The high frequency furnace is started to heat the graphite crucible and the blank value of the measured graphite crucible and flux (tin) are deducted in the analysis results. The blank should be measured more than three times so as to guarantee blank stability. The blank measuring conditions are the same as the sample analysis conditions.

Sample analysis: a clean tweezers is used to add the weighed analytical sample joined with the flux into the graphite crucible with the gas. The carrier gas is used to rinse the furnace and then the small high frequency furnace is started to heat the melted sample. The heating temperature is above 2,000°C and the time is 40 seconds. The hydrogen (including carbon monoxide and nitrogen) released in the sample is measured after it joins with the carrier gas and enters the chromatographic heat conducting pool. It records the peak and deducts the blank so that the peak calculates the hydrogen content.

#### 5. Calculations

The analysis results were calculated according to the following formula:

$$[H]\% = \frac{K \cdot V}{G} \times 100$$

In the formula: K is the hydrogen when the constant and temperature pressure coefficient is multiplied by the standard conditions; V is the volume (milliliters) of the hydrogen

released in the sample: G is the weight (grams) of the test piece.

#### 6. Drawing the Standard Curve

We measure the peaks of pure hydrogen gas of 0.05, 0.10, 0.15 and 0.20 milliliters under the same conditions as the analytical sample so as to (? illegible) and draw the standard curve. We can also use a sample with a known hydrogen quantity to analyze and measure the peak and draw the standard curve.

#### 7. Allowable Deviation

Hydrogen Content (ppm)	Allowable Relative Standard Deviation %
< 50	5
> 50	10

Note 1: After many years of actual analysis the sensitivity of this method can reach 0.1-0.3 ppm, the analytical range 10-200 ppm and if the contents exceed 200 ppm this can reduce the weight of the sample.

Note 2: A one thousand watt small high frequency furnace is used as the heating source for inert gas melting-gas chromatography. When considering certain units, we use a heating source in the same way. Yet, the temperature of the melted sample must be controlled.

Note 3: The graphite crucible is made of a spectrum pure graphite electrode. Its measurement and size can be selected based on the apparatus used. This method uses a crucible shape as shown in fig. 3.



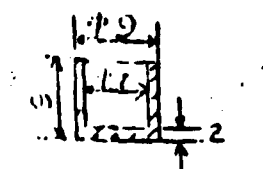


Fig. 3 Shape and Measurement of the Graphite Crucible

STANDARD FOR THE DETERMINATION OF OXYGEN  
IN TITANIUM AND TITANIUM ALLOYS

(The Beijing Institute of Aviation Materials)

The Pulse Heating - Coulomb Analytical Method

1. Summary of Method

When a titanium or titanium alloy sample is in a pure hydrogen atmosphere, there is carburization melting in the graphite crucible with a nickel or nickel-tin bath created at high temperature ( $> 3,000^{\circ}\text{C}$ ). The oxygen in it is separated out of the carbon monoxide and it is heated by the argon carrier gas flow to a  $450\text{--}500^{\circ}\text{C}$  copper oxide furnace tube and transformed into carbon dioxide. This goes into the barium perchloric acid main beaker absorbent of the Coulomb analyzer causing the acidity to change. After going through a Coulomb electrolytic pool, barium hydroxide was produced in the negative pole causing the absorbent to restore the original acidity (pH value). The carbon dioxide's absorbancy was derived from the consumed quantity of electricity in the electrolytic process and the method of recording the Coulomb quantity was used to display the oxygen content in the sample.

The oxygen determination range of this method was:

Pure titanium oxygen content [O] %: 0.10-0.40.

Titanium alloy oxygen content [O] %: 0.02-0.20.

## 2. Reagent and Implements

The main beaker of absorbent: 50 grams of barium perchloric acid are dissolved in 1,000 milliliters of double distilled water and added into 30-50 milliliters of isopropyl alcohol, dissolved and shaken evenly;

The secondary beaker solution: 50 grams of analyzed pure barium perchloric acid are dissolved in 250 milliliters of double distilled water and shaken evenly;

The small beaker solution: 5 grams of analyzed pure barium perchloric acid and 3 grams of analyzed pure sodium chloride are dissolved in 100 milliliters of double distilled water and a 5% silver nitrate solution is dripped in. After being heated to 60-70°C and then cooled, the upper layer of clean solution is used;

Barium perchloric acid: analytically pure;

Barium carbonate: analytically pure after grinding;

Silver nitrate: analytically pure;

Isopropyl alcohol: analytically pure; at 500-700°C

Copper oxide: filiform, placed in a quartz furnace tube. The quantity released after the argon burns to oxygen is less than 2 micrograms/minute; used when it drops to 450-500°C;

Ether : analytically pure;

Acetone : analytically pure;

Materials: electrolytic nickel or another pure nickel (> 99.5%);

Tin : tinfoil or tin particles;

Stopwatch : graduation 1/100;

Balance : 1/10,000 induction quantity;  
Crucible or sample clamp: a stainless steel product;  
File : fine-tooth file;  
Ear ball : rubber, should be large but one is small;  
Standard carbon monoxide gas: density already determined.

### 3. Apparatus

Pulse heating - the Coulomb gas fixing instrument is composed of the following sections:

Pulse dissolving furnace: composed of oxygen-free copper in two electrodes which depend on fixed processing. When used, water cooling should be employed so that the graphite crucible operates normally when passing into a 0-1,000 ampere current;

Coulomb absorption pond: composed of a main beaker absorption pond, glass electrode (231), a secondary electrode beaker, a small beaker (silver-silver chloride electrode) and platinum electrode. The glass electrode and silver-silver chloride electrode compose an indicator electrode and the two platinum electrodes compose an electrolytic circuit by the secondary beaker. Its action guarantees that the acidity brought about after the full absorption of the carbon dioxide will change and cause it to attain an electrolytic balance;

Numerical display: each number is  $6.03 \times 10^{-8}$  coulomb, equivalent to  $0.5 \times 10^{-6}$  grams of oxygen;

Gas path control section: the bottle with argon gas regulates the flow by a decompression valve and after passing the molecular sieve, and sodium asbestos and phosphorus pentoxide,

it enters the pulse furnace. The released gas is carried past the dust arrestor and after being heated in the 450-500°C copper oxide revolving furnace it enters the Coulomb absorption pond; when the graphite crucible pushes the gas out, the gas path should change to the exhaust gas path;

Electric control section: the pH value of the electric section is controlled by the microvolt meter. After the electrolyte current is measured by the potentiometer through the milliamperemeter a suitable value is selected; the careful regulation procedure and method should be carried out according to the directions for a KLS-56 coulomb analyzer.

The instrument's structure and flow chart are as follows:

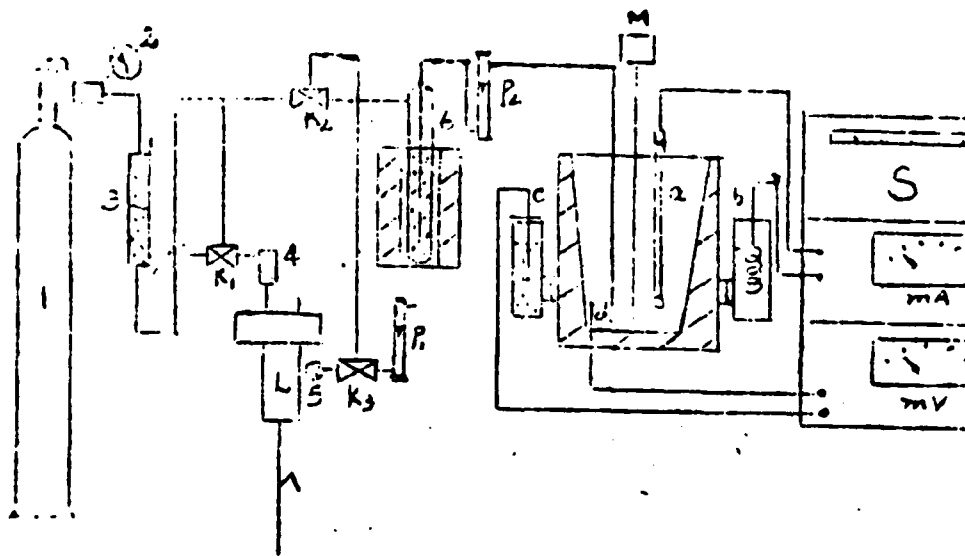


Fig. 1

Fig. 1 Schematic of the Structure and Gas Path of the Pulse Heating - Coulomb Oxygen Fixer

1. Argon gas bottle
2. Decompression valve
3. Molecular sieve with sodium asbestos
4.  $P_3O_5$  drier
5. Dust arrestor
6. CuO revolving furnace
- $K_1K_2$ , K two tee joint electromagnetic valves
- L, pulse heating furnace
- $P_3P_2$ , current meter
- M, mixer
- a, glass electrode
- b, small beaker (Ag-AgCl electrode)
- c, secondary beaker ( $Na_2CO_3$  + Pt electrode)
- d, Pt pole
- S, numerical display (electrode regulation section)

#### 4. Analysis Procedure

##### 4.1 Preparation of Sample:

The titanium and titanium alloy sample lathe has a diameter of 2 millimeters, a smooth cylinder with a length of 3 millimeters and other neat shapes. A fine file is used to file a new surface on the sample and then use analytically pure ether and acetone to carefully rinse and blow it dry. We use an analytical balance for weighing and in sequence store them in containers. Further, we also carry out the same cleaning process and driving for the pure nickel and tin bath material.

##### 4.2 Apparatus Correction.

In order for the analysis results to be accurate and reliable, we must use various methods to correct the numerical display. Generally, we can use electric quantity correction, perchloric standard solution titration, carbon monoxide or carbon dioxide standard gas recovery tests and tungsten trioxide or standard

sample analysis. If conditions do not permit this, we must also carry out electric quantity correction and standard sample analysis tests so as to determine the accuracy of the analysis values.

#### 4.3 Blank Measurement

The final design of the graphite crucible is placed between the two electrodes of the pulse furnace. The electrode must be fully water cooled and when entering the flow of the pure argon, the electric source causes the graphite crucible to push out gas for 20 seconds under a high temperature ( $> 3,000^{\circ}\text{C}$ ) based on the bath ratio added into the bath material. When the gas exhausts for 20 seconds under the analysis sample temperature, we further heat the crucible for 15 seconds to measure the blank value. This value should be smaller than 10 micrograms/2 minutes. After the blank value is steady, it is smaller than 15 micrograms/2 minutes so that we can carry out sample analysis. This blank value should be deducted from the total display value.

#### 4.4 Sample Analysis

Use a clean tweezers to place the cleaned and weighed sample in the pulse furnace head's sample hole pushing and aiming at the crucible position turning  $180^{\circ}$ . The specimen can be dropped into the crucible and then we turn on the electric source switch and heat and melt the sample for 15 seconds. The oxygen in the sample is reduced by the carbon so as to separate out the carbon monoxide. It is quickly guided by the argon

carrier gas and heated in the 450-500°C copper oxide revolving furnace and then enters the main beaker's absorbent. At this time, the carbon dioxide is absorbed by the mixed barium perchloric acid solution. The resultant acid changes and is neutralized by the pulse electrolyte alkalinity. A corresponding numerical display is used to calculate the results. When the jump number reaches the blank value the test can be completed. If a crucible is continuously used for analyzing the sample, each analysis of a sample must supplement over 0.2 grams of bath material. At the same time, it is necessary to exhaust so as to carry out blank tests and further analyze the sample. It is only necessary that the crucible and temperature be suitably selected for us to be able to use a crucible to analyze 1-4 samples; in most situations, one crucible can analyze one sample.

#### 4.5 Analysis Conditions

Use of pulse heating - the Coulomb analysis method determines the oxygen in titanium and titanium alloys. The apparatus should attain the following indices:

Analysis time	: 5%
Apparatus sensitivity:	0.5 micrograms of oxygen
Analysis time	: 2-3 minutes
Pulse heating temperature	: ~ 3,000°C
Carrier gas flow speed	: 200-300 milliliters/minute
Weight of sample	: 0.02 - 0.10 grams



### 5. Calculations

The percentage content of oxygen is calculated by the following formula:

$$[O]\% = \frac{0.5 \times 10^{-6}}{G} (A - Bt) \times 100$$

In the formula: A is the count when specimen analysis is finished; B is the count (count/minute) of the blank value; t is the analysis time (minutes);  $0.5 \times 10^{-6}$  is the oxygen quantity (grams) corresponding to each count; G is the weight (grams) of the sample.

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